ELECTROCHEMICAL STUDIES OF REDUCIBLE AROMATIC COMPOUNDS

BY

ROBERT EDWARD VISCO
B.S., University of Wisconsin, 1955
M.S., University of Wisconsin, 1957

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Chemistry
in the Graduate College of the
University of Illinois, 1963

Urbana, Illinois

UNIVERSITY OF ILLINOIS

THE GRADUATE COLLEGE

OCTOBER 6, 1962

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY ROBERT EDWARD VISCO

ENTITLED ELECTROCHEMICAL STUDIES OF REDUCIBLE AROMATIC COMPOUNDS

BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

Howard V Malmstadt
In Charge of Thesis

H. S. Carter
Head of Department

Recommendation concurred in†

B. P. Susard
Arnold M. Hawley
Leon Kuppenheim
Peter E. Yankwich

Committee on Final Examination†

† Required for doctor's degree but not for master's

D517

ACKNOWLEDGMENT

I wish to express my sincere thanks to Dr. Arnold M. Hartley for suggesting this problem, and for his continued guidance throughout the course of this work. I am also greatly indebted to Dr. Charles S. Johnson for the many hours he spent during the course of the electrochemical-ESR experiments and to my fellow graduate students for their many scientific discussions and helpful comments. I wish to thank the State of Illinois, The Electrochemical Society, and the National Science Foundation for financial assistance during the course of this study.

Both to my parents for their continued encouragement during this long education process, and to my wife, Peggy, for her self-denial, patience, and encouragement I owe a debt beyond measure.

TABLE OF CONTENTS

I. INTRODUCTION

"An assumed state becomes real when its properties are measured,"

G. N. Lewis and M. Kasha

Electrochemistry is the study of reactions which take place at an electrode-solution interface. The course of such reactions can be described by appropriate electrochemical mechanisms. The variables which are available to characterize the electrochemical mechanism are current, electrode potential, and time. Time is always an independent variable while either current or potential is the dependent variable. Heterogeneous electrochemical kinetic schemes like chemical kinetic schemes can be better understood by a complete chemical analysis of major and trace products. The presence of transitory intermediates in an electrochemical scheme is usually hypothesized. The existence of such intermediates is inferred from the current-potential-time behavior of the particular electroactive species or from the products observed rather than from an independent characterization of these intermediates.

The electrochemist experiences a major difficulty in transforming his experimentally observed functional relationship of current potential and time into a functional relationship of concentrations and time. Since the electrochemical mechanism involves at least one heterogeneous step, a model for the transport of species between the bulk of solution to the region of the electrode-solution interface is necessary. Current at any given potential being the algebraic sum of all cathodic (reduction) and anodic (oxidation)

processes, the transformation of the measured net variable into concentrations and fluxes is a fundamental difficulty. This difficulty is similar to that encountered when one measures a colligative property.

The difficulty of transforming a net variable and the usual inability to isolate and characterize transitory intermediates has led to ambiguity in the interpretation of electrochemical phenomena. This has left much to be desired in the detailed mechanistic description of many electrochemical reactions.

Demonstration of the existence and the importance of certain types of transitory intermediates in an electrochemical kinetic scheme by a non-electrochemical measurement is now possible. The existence and importance of molecules with umpaired spins in an electrochemical process can be demonstrated by simultaneous electrochemical and electron spin resonance (ESR) measurements. By studies of the nature and intensity of the ESR absorption spectrum and its relation to the usual electrochemical variables, it should be possible to elucidate the role in the electrochemical mechanism played by species with unpaired spins.

This thesis is an effort to apply electron spin resonance spectroscopy to the study of in situ electrochemically generated transitory and stable organic free radicals. The hope is to obtain a better understanding of the role played by these free radicals in electrochemical processes.

II. HISTORICAL

Polarography is a very useful tool for examining electrochemical processes. Numerous reductions and oxidations have been examined polarographically since Heyrovsky first reported such phenomena at a dropping mercury electrode[1]. The early studies of organic systems were restricted to morphological description of the polarographic wave rather than mechanistic definition of the processes taking place at the electrode-solution interface.

An electrochemical mechanism must of course start with a statement of the overall process, i.e., the number of protons, solvent molecules and electrons added to or removed from the electroactive substance. If the process involves several electrons, there will usually be more than one electron transfer step. There may be steps involving protonation, dehydration, etc., some of which may be slow. These chemical steps may also be slow relative to the slowest electron transfer step. The state of the electrode surface with respect to sorption of reactants, products or other molecules as well as the configuration of the sorbed molecule must also be described. The electron transfer steps must be described, that is, whether the transfer is completely reversible, totally irreversible or if neither, the degree of irreversibility must be stated. The order of each of the chemical reactions, the configuration of the activated complex, and the chemical steps preceding the rate determining step must all be elucidated.

Such detailed descriptions of electrochemical mechanisms have as yet

not been reported, but certain fundamental steps have been taken. Numerous mechanisms have been proposed; several are shown and discussed below. Starting with some early work of Evans and Hush [2], Elving and Pullman [3] have recently proposed a very general mechanistic scheme which seems to fit most cases and possesses a degree of simplicity and rationality which allows it to be extremely useful and versatile.

A major effort of the Czechoslovakian school of polarography has been directed at describing the polarographic current-potential-time characteristics of reactions with slow chemical and slow electrochemical steps [4,5]. Reinmuth and coworkers [6,7] have recently presented an analogous treatment of potential-time curves for similar systems studied chronopotentiometrically (voltammetry at constant applied current).

The cases discussed below will all be organic reductions, but this does not imply that the same problems are not encountered in organic oxidations or both inorganic oxidations and reductions.

Laitinen and Wawzonek [8] proposed a mechanism for the reduction of styrene and stilbene which was pioneering and provocative,

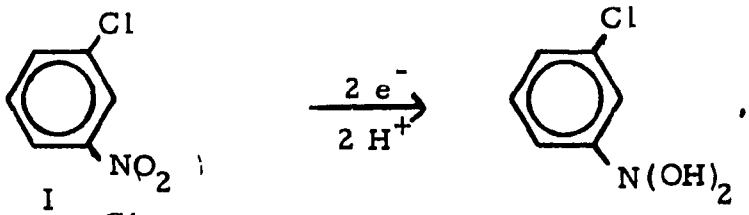
$$R + 1\ e^- \longrightarrow R^- \qquad \text{(reversible, potential determining)}, \quad (1)$$

$$R^- + 1\ e^- \longrightarrow R^= \qquad \text{(irreversible)}, \quad (2)$$

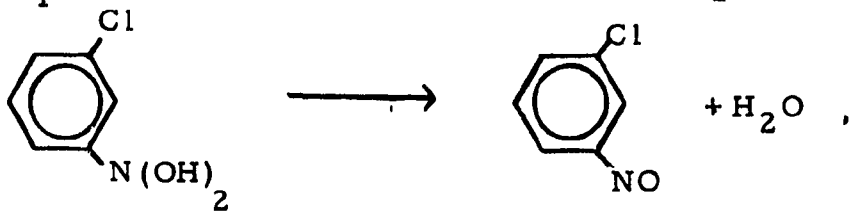
and

$$R^= + 2\ H_2O \longrightarrow RH_2 + 2\ OH^- \qquad \text{(irreversible, rapid)}. \quad (3)$$

Clark [9] has recently proposed the following mechanism for the reduction of m-chloronitrobenzene, I,

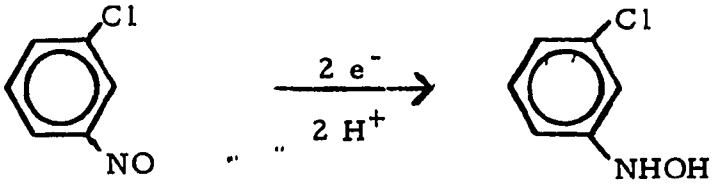


I (4)



(5)

and

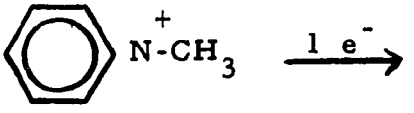


(6)

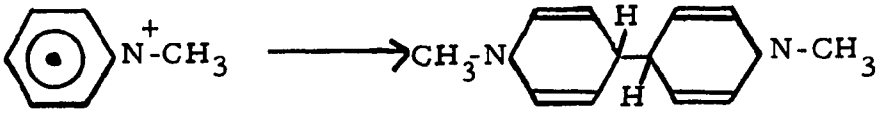
This is in essential agreement with the mechanism proposed earlier by Kroshunov and Kirellova [10]. Clark has also obtained evidence that the second electron is added slowly with respect to the first electron. It has recently been shown that no chemical steps precede the first electrochemical steps [11], and therefore, it has been proposed that the first electron addition in the reduction of an aromatic nitrocompound is potential determining. This requires that there be a finite concentration of $ArNO_2^-$ existing during the course of the electrolysis. Kemula [12] has offered oscillopolarographic evidence for several transient intermediates in the overall four-electron reduction of $ArNO_2$. One intermediate suggested was $ArNO_2^-$. In the aprotic solvent, acetonitrile, Maki and Geske [13] have shown by using electrochemistry and electron spin resonance spectroscopy that the most anodic reduction process for $ArNO_2$ is a one-electron reversible reduction yielding $ArNO_2^-$. Piette, Ludwig and Adams [14,15] have recently shown that even in aqueous solution during the electrochemical

reduction of aliphatic and aromatic nitrocompounds, there is a finite concentration of RNO_2^-. They detected the existence of these radicals by electron spin resonance spectroscopy. Experimental details as to electrode potential and relative current efficiency for radical formation were not reported by these authors.

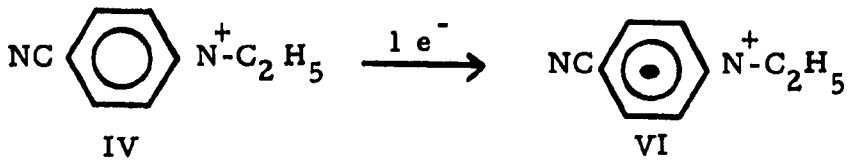
The polarographic behavior of N-methylpyridinium ion, II, studied by Tompkins and Schmidt [16], indicates a one-electron reduction to a free radical, III. Controlled potential electrolysis [17,18] suggests that this initial radical couples in the 4 position as shown below:



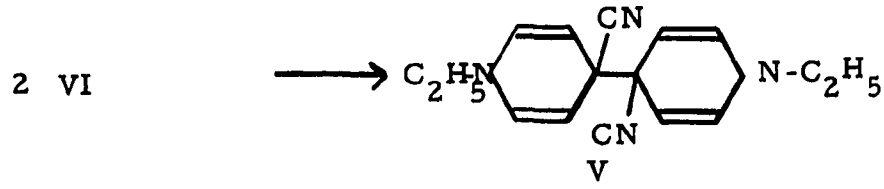
II III (7)

and 2  (8)

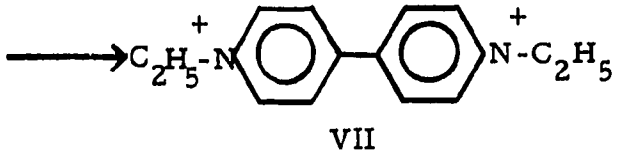
Recently Schwarz, Kosower and Shain [19] have studied the electrochemistry of 4-cyano-1-ethylpyridinium ion, IV, and have shown that the condensed product, V, formed by condensation of the 4-cyano-1-ethylpyridinium radical, VI, eliminates two cyanide ions and produces N, N'-diethyl-4, 4'-dipyridyl, VII. This ion, VII, is reducible at potentials necessary to reduce the original 4-cyano-1-ethylpyridinium ion, IV. The reduction of VII is a reversible one-electron process and yields the N, N'-diethyl-4, 4'-dipyridyl radical ion, VIII. The proposed mechanism is shown below:



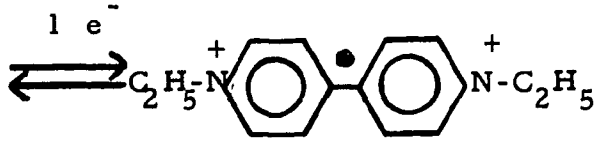
IV VI (9)



V (10)

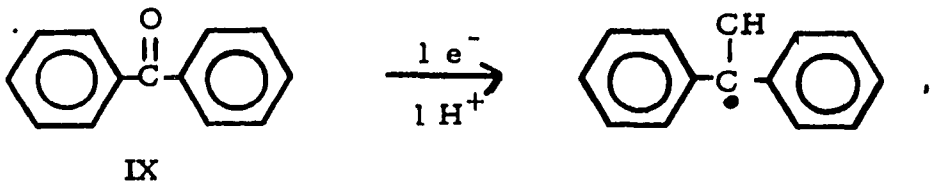


VII (11)



VIII (12)

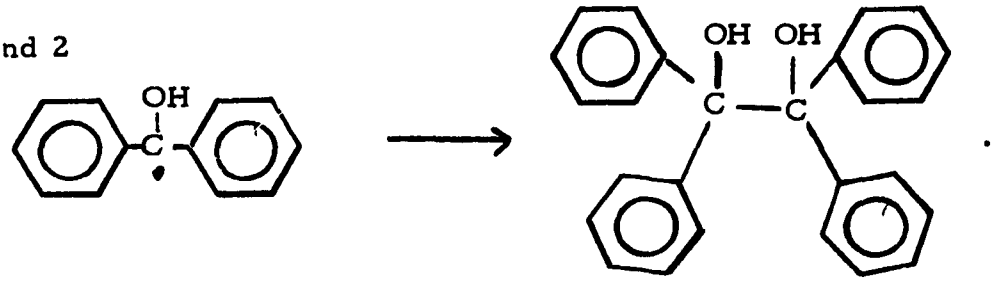
'The polarographic reduction of certain aromatic aldehydes and ketones in acidic solutions has long been thought to involve a one-electron reduction with a subsequent coupling of two free radicals to yield the corresponding pinacol [20]. The polarography in acidic solution is characterized by two reduction processes. The most anodic is believed to be the one-electron reduction, followed at more cathodic potentials by a direct two electron reduction to the corresponding alcohol. Controlled potential electrolysis at potentials corresponding to the diffusion plateau of the first wave yields the corresponding pinacol [21]. Suzuki and Elving [22] have proposed the following mechanism for the first reduction process of benzophenone IX:



IX

(13)

and 2



(14)

The several mechanisms given above are typical of those proposed for other electrochemical reductions. They have at least three features in common. First, all require a mass transport of the electroactive species from the bulk of solution to the electrode surface. Second, there is at least one heterogenous electron transfer step. Third, there are as a rule two classes of chemical reactions which presumably take place. The first type is believed to take place in the immediate vicinity of or directly on the surface of the electrode. The second class is believed to take place at distances from the electrode surface which are large when compared to the distance at which the concentration of the electroactive species has essentially reached its bulk concentration. The products of this second type of chemical reaction may be electroactive, but because of their distance from the electrode surface they must be transported to the vicinity of the surface before they can participate in another heterogenous electron transfer step.

Mass transport processes can be considered to be of three types: migration of charged species in a potential gradient, convection or agitation

due to density or thermal gradients or a relative motion of the electrode with respect to the solution, and diffusion under the influence of a concentration gradient. Most electrochemical experiments are designed to minimize migration through the addition of a diverse or indifferent electrolyte. Studies in stirred solution or where convection is important can be in some cases described with mathematical rigor [23]. The equations necessary to describe diffusion depend on electrode geometry and are similar to those used for heat flow in solids. There is ample evidence of agreement between diffusion theory and electrochemical experiment [24,25,26].

Delahay [27,28] has reviewed and examined the current-potential-time behavior of electrochemically reversible and irreversible processes. This author has chosen to define a reversible process as one "where the electrochemical reaction is so rapid that electrochemical equilibrium is achieved at the electrode, . . . and the Nernst equation can be applied in the calculation of the electrode potential." Irreversible processes have been described by absolute rate theory. The relevant equation is given below:

$$i = nFAC_{ox}k^{o}_{fh}\exp\left[\frac{-\alpha n_a F}{RT}(E-E^{o'})\right] - nFAC_{red}k^{o}_{bh}\exp\left[\frac{(1-\alpha)n_a F}{RT}(E-E^{o'})\right], \quad (15)$$

where i is current, n, the overall number of electrons transferred per molecule of oxidant or reductant, F, the Faraday, A, the area of the electrode,

C_{ox} and C_{red}, are the surface concentrations of the oxidant and reductant, k^{o}_{fh} and k^{o}_{bh} are the heterogenous electron transfer rate constants at the formal potential of the couple, $E^{o'}$, n_a is the number of electrons in the slow electron transfer step, E is the applied potential, T is the absolute temperature, and α is a parameter whose value is between 0 and 1. The parameter, α, can be defined in several ways, but its most descriptive meaning is the fraction of the total energy, $-nF\Delta E$, that acts to decrease the height of the cathodic energy barrier or essentially drive the cathodic reaction. Thus α may be interpreted as a measure of the symmetry of the energy barrier [29].

Totally irreversible electrochemical reductions are cases in which the back reaction is negligible at the particular applied potential and therefor one term of (15) can be neglected. Cases in which the electrochemical equilibrium is not rapidly established, but where the back reaction is important are considered to be partially irreversible. The current as a function of concentration and potential can only be described by use of both terms of (15).

The mechanism proposed by Evans and Hush [2] is of interest because these authors realized many of the possible fates of electrochemically reduced products. They considered the one-electron reduction of AB resulting in cleavage of the AB bond,

$$AB \xrightarrow{1\ e^-} A^- + B. \qquad (16)$$

They then listed several possible chemical fates of A^- and B, namely, dimerization, electron transfer and proton transfer.

$$A^- + A^- \longrightarrow A^= + A\,, \tag{17}$$

$$2A^- + 2H_2O \longrightarrow (AH)_2 + 2\,OH^-, \tag{18}$$

$$A^- + H_2O \longrightarrow AH + OH^-, \tag{19}$$

$$B + B \longrightarrow B_2\,, \tag{20}$$

and

$$B + B \longrightarrow BH_2 + (B - H_2). \tag{21}$$

Of the several possible electrochemical fates of A^- and B, they chose to consider only the reduction of B,

$$B \xrightarrow{1\,e^-} B^-. \tag{22}$$

Since their interest was in the reduction of alkyl halides, Evans and Hush set aside consideration of the chemical complications and only considered in detail the electrochemical steps given above, (16) and (22).

From the viewpoint of the proposition of general electrochemical mechanisms, their chief contribution was a realization of the many possible chemical complications which can arise after a heterogenous electron transfer. The electrochemical case considered by Evans and Hush was simplified considerably since a multielectron reduction was not postulated, and therefore the relative ease of successive electron addition did not have to be considered.

Elving and Pullman [3] have postulated a series of reactions, both chemical and electrochemical, which they feel will be most useful in describing organic electrochemical mechanisms. The several steps are given

below and are shown in a more schematic fashion in Figure I,

$$R\text{-}X + e^- \pm (H^+, OH^-, H_2O) \longrightarrow \text{electrode complex}, \quad (23a)$$

$$\text{electrode complex} \longrightarrow [R\cdot] + X^- \pm (H^+, \text{etc.}), \quad (23b)$$

$$[R\cdot] \longrightarrow R\cdot, \quad (24)$$

$$R\cdot + R\cdot \longrightarrow R\text{-}R, \quad (25)$$

$$R\cdot + e^- \longrightarrow (R:)^- \pm (H^+, \text{etc.}), \quad (26)$$

$$[R\cdot] + e^- \longrightarrow (R:)^- \pm (H^+, \text{etc}), \quad (27)$$

$$(R:)^- + H^+ \longrightarrow RH \pm (H^+, \text{etc.}), \quad (28)$$

and

$$(R:)^- \longrightarrow (\text{electronic rearrangement products}) \quad (29)$$

The species $[R\cdot]$ is unstable radical but can be converted to the stable radical $R\cdot$.

The case of multiple bonded reactants can be described by the following step where Z is some solvent component:

$$R\text{-}X + e^- \quad [R\cdot\!-\!X] \pm (H^+, \text{etc}), \quad (31)$$

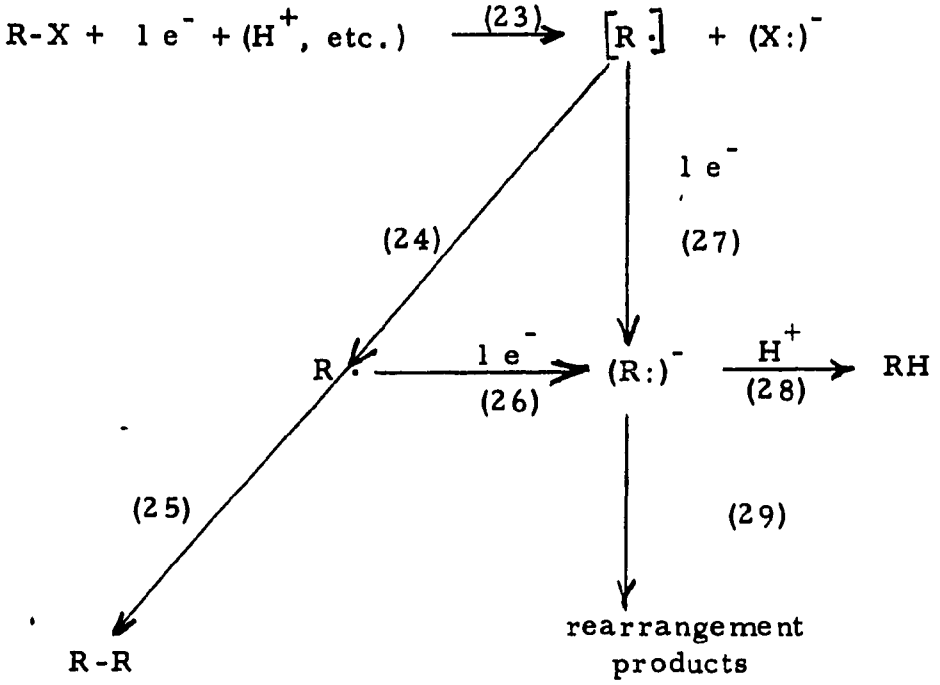
and

$$R\text{=}X + e^- + Z \quad [R\cdot\!-\!X\text{-}Z] \pm (H^+, \text{etc.}). \quad (32)$$

Cases in which the first electron does not result in R-X bond fission are described by (31) and (32).

The intermediate species $[R\cdot\!-\!X]$ and $[R\cdot\!-\!X\text{-}Z]$ may be converted to the stable free radicals $R\cdot\!-\!X$ and $R\cdot\!-\!X\text{-}Z$ or further reduced to a carbanion.

Figure I



Schematic of the Elving and Pullman [3] generalized electrochemical reaction mechanism for the case of single electron transfer steps and R-X bond fission. Equations are numbered as in the text.

There is now a possible path for multielectron transfers since two electrons have already been added to reach a carbanion. The rearranged product of the carbanion may also be reduced at the particular applied potential. Much imagination is not needed to conceive a variety of fates for the initial products of the multiply-bonded structures. The species $R^{\cdot}$—X-Z or $R^{\cdot}$—X could easily accept with varying degrees of rapidity additional electrons or undergo any of the several chemical steps already presented.

Considering the mechanism of Laitinen and Wawzonek [8] in terms of the above general mechanism, it is apparent that when expressed in the terms Elving and Pullman , this is a particular example of (23), (27), and (28).

The early steps in the mechanism for aromatic nitrocompounds proposed by Clark [9] are in reality (23) and a combination of (27) and (28). If one could show that the intermediate observed by Kemula [12] was $ArNO_2^-$, then (24) must also be included.

The case of 4-cyano-1-ethylpyridinium ion reduction [19] can be described by (23), (24) and (25). Considering R-R as a new electroactive species, since it results from a chemical reaction taking place in the bulk (25), the remainder of the mechanism is described by (23) and (24).

The case of the first reduction wave for carbonyl compounds in acid solution can be described by (23, (24) and (25).

In order to demonstrate that a proposed electrochemical mechanism is consistent with experiment, it is necessary to calculate current-potential-time curves for the system considering mass transport and the chemical and electrochemical steps. A comparison of calculated and observed curves

then forms the basis for a value judgment of the mechanism under consideration. Such calculations have been performed and the general considerations are discussed and reviewed by Delahay [30]. Several polarographic examples of the Czechoslovakian school have been recently discussed [4,5]. Numerous equations of potential-time curves for electrolysis at constant applied current, chronopotentiometry, have been given by Reinmuth [6,7].

The general procedure for a given proposed mechanism, [30], is to write down the appropriate diffusion equation including any chemical complications, the necessary initial, and boundary conditions and solve the resulting partial differential equation. The solution will hopefully be in a closed form and should relate the electrode potential, electrolysis current, concentration, number of electrons, area of the electrode, and time. A very simple mechanism having no chemical complications, but involving an irreversible reduction is shown below:

$$O_{bulk} \xrightarrow{\text{diffusion}} O_{surface} \xrightarrow{1\ e^-} R_{surface} \xrightarrow{\text{diffusion}} R_{bulk} . \tag{33}$$

The solution of the boundry value problem assuming linear diffusion to a planar electrode and an irreversible reduction has been reviewed by Delahay [28] and is shown below:

$$\frac{i}{i_d} = \pi^{\frac{1}{2}}\lambda \quad \exp(\lambda^2)\,\operatorname{erfc}(\lambda) \tag{34}$$

where

$$\lambda = \frac{t^{\frac{1}{2}}}{D^{\frac{1}{2}}} \quad k^o_{fh} \quad \exp\left[\frac{-\alpha n_a F}{RT} \quad (E-E^o)\right], \tag{35}$$

The quantities (i) and (i_d) are the currents at potentials where the surface concentration of (0) is respectively greater than zero or essentially zero. The function erfc is the complement of the error function. The other notation has been previously defined.

The usual problem with such solutions is that for cases with chemical complications much chemical intuition is necessary to write down a mechanism. Of more importance is that the test of calculated versus observed current-potential-time data usually forms the sole basis of judging the acceptability of the mechanism. It would be convenient if some chemical intermediates could be isolated and characterized. The potentials where these intermediates occur and the current efficiency for their formation would aid significantly in characterizing the mechanism. Unfortunately, because of the rather restricted geometry of a dropping mercury electrode and the small fraction of an exhaustive electrolysis taking place, techniques independent of electrochemistry have not been widely applied.

Beronius [31] has recently used deposition of a radioactive tracer to study diffusion layers in stirred and quiet solutions. This technique is applicable to the study of the electrode and material deposited on it, but appears to be of little use in studying chemical and electrochemical processes taking place on the solution side of the electrode-solution interface.

Maki and Geski [13] have generated in acetonitrile at mercury micropool electrodes the one-electron reduced free radicals of several nitroaromatic compounds and they have reported the electron spin resonance (ESR) absorption spectra of these compounds. The fundamental contribution was

the in situ electrochemical generation of these radicals and the simultaneous recording of their ESR spectra during electrolysis. It is true that the radical is the final stable product of the electrolysis, but the simultaneous employment of an independent measuring technique with electrochemistry is the important advance. Ingram and coworkers [32] had already used electrochemical generation of radicals, but he transferred the radical from the electrolysis vessel to the cavity of the spectrometer and therefore he did not simultaneously perform both measurements. Using the technique of Maki and Geski [13], Piette, Ludwig and Adams [14,15] have reported the observation of transient radicals in the electrochemical reduction of aliphatic and aromatic nitrocompounds. They reported the observation of radicals in acetate buffers, neutral buffers, strong base and unbuffered solutions. These authors did not report the electrode potential relative to the polarographic half-wave potential nor did they report the relative current efficiency for radical formation. Nevertheless the observation by a technique independent of electrochemistry, that there are organic radicals which can exist in aqueous solution with a half-life of seconds to minutes is in itself a fundamental advance.

The electrochemist now has an independent tool which will allow him to determine the existence of a certain class of transient or stable electrochemically generated species. This type of information should be exceedingly useful in elucidating the course of many electrochemical processes.

III. THEORETICAL

A. Electron Spin Resonance Absorption Spectroscopy

Electron spin resonance and spectroscopy, ESR, is a useful tool in the study of atoms and/or molecules which have unpaired electrons. The reader is referred to the text by Ingram [33] for a more complete discussion. The following discussion will be restricted to liquids in which molecular motions are sufficiently rapid to reduce to zero the anisotropic components of electromagnetic interactions. It is further restricted to molecules in which the coupling between the orbital angular momentum and the spin of the electron is highly quenched. In such systems the electron is essentially "free". Most organic "free radicals" fall into this class.

Hyperfine splittings are useful in characterizing ESR spectra. These splittings result from interactions between the magnetic moment of the unpaired electron and the magnetic moment of nuclei which are embraced in the molecular orbital of the unpaired electron. The mathematical relation expressing the energy of interaction is the "Hamiltonian", for the case of isotropic splitting the Hamiltonian can be written as:

$$\mathcal{H} = g_e g_N \beta\beta_N \left[\frac{-8\pi}{3} S_e I_N \delta (r_e - r_N)\right]. \qquad (36)$$

where (g_e) and (g_N) are the (g) factors for the electron and the nucleus respectively, (β) and (β_N) are the Bohr magnetons for the electron and the nucleus, (S_e) and (I_N) are spin operators for the electron and the nucleus, and $\delta(re - r_N)$ is the Dirac delta-function for the distance between the electron and the nucleus, normalized in three dimensions. The Dirac

delta-function will have a non-zero value only if the molecular orbital occupied by the unpaired electron does not vanish at the position of the nucleus. Only molecular orbitals with sigma symmetry, have a finite probability for the electron wave function at the nucleus. Molecular orbitals with π symmetry have a node at the nucleus; thus only electrons which are in σ molecular orbitals have the ability to produce isotropic hyperfine splittings. Unpaired electron density can be distributed from the π system of the aromatic "free radical" to the peripheral atoms via the mechanisms of configuration interaction [34] and/or hyper-conjugation [35]. Further it has been shown [36] that the magnitude of the observed hyperfine splitting, the coupling constant, produced by an atom with a magnetic moment is linearly related to the unpaired electron density at the nucleus.

In the event that no two nuclei in a molecule are equivalent, the maximum number of lines in an ESR spectrum in $\prod_{s_i=1}^{n}(2I_i + 1)$, where I_i is the maximum value of the nuclear spin of the i^{th} atom in a molecule with (n) atoms in units of $h/2\pi$. In the case of (j) equivalent atoms, I_i is the vector sum of the maximum value of the nuclear spin for the (j) equivalent atoms. If all the I_i's are integers, then a line will be observed in the center of the ESR spectrum. If one or more of the I_i's is not an integer but is a fraction, then no line will exist in the center of the spectrum. There will always be a point of inversion in the center of the ESR spectrum of a free radical regardless of the particular values of the several I_i's.

The number of lines observed in the ESR spectrum for a given free radical will never be greater than $\prod_{i=1}^{n}(2I_i + 1)$, but it may be less than this

number. The usual reason for observing less than the theoretical number of spectral lines is that several coupling constants are simple multiples of each other.

The synthesis of ESR spectra is discussed in chapter 1 of the text by Ingram [33].

From the viewpoint of electrochemistry ESR spectra have two useful features. The first is that spectra yield a consistent set of coupling constants which can be used to characterize the free radical. Second, the intensity of the signal can be used to determine the number of unpaired spins present in the cell.

Ingram [33] has described two schemes for the determination of the number of unpaired spins in the test volume within the microwavecavity. He has outlined an absolute calibration of the spectrometer employing appropriate equations and instrument parameters. He has also described a relative calibration against a sample containing a known number of unpaired spins. For the latter scheme he suggests as a standard the stable radical, 1,1-diphenyl-2-picrylhydrazyl which has one unpaired electron per molecule.

B. Consideration of Consecutive One-Electron Electrochemical Reductions

Several possible cases for an overall two-electron reduction are shown below:

$$O \overset{1e^-}{\rightleftharpoons} Z \overset{1e^-}{\rightleftharpoons} R, \tag{37}$$

$$O \overset{1e^-}{\rightleftharpoons} Z \overset{1e^-}{\longrightarrow} R, \tag{38}$$

$$O \overset{1e^-}{\longrightarrow} Z \overset{1e^-}{\rightleftharpoons} R, \tag{39}$$

and

$$O \overset{1e^-}{\longrightarrow} Z \overset{1e^-}{\longrightarrow} R. \tag{40}$$

The double arrows signify a reversible process. A single arrow signifies an irreversible step where the back reaction is negligible at the potentials of interest. These four cases consider only electrochemical steps and do not consider the possible chemical fates of Z and R. The notation used is that of Berzins and Delahay [37]. The species Z would be a free radical while R would be a carbanion. Equations (37) to (40) in the notation of Elving and Pullman [3] would correspond to (23) and (26) or (27).

For the above cases let us consider the qualitative features of the current-voltage curves at a dropping mercury electrode. In all four cases these curves would have two breaks if the potential-dependent rate for the second electron transfer is small compared to the first when referred to a common reference potential. Each break could be described by the appropriate current-potential-time equation for either a reversible or irreversible process. The reversible case is described by (41) which was derived by Heyrovsky and Ilkovic [38],

$$E = E^{o} + \frac{RT}{nF} \ln \left[\frac{f_o D_r^{\frac{1}{2}}}{f_r D_o^{\frac{1}{2}}} \right] + \frac{RT}{nF} \ln \left[\frac{i_d - i}{i} \right], \qquad (41)$$

where (f) is an activity coefficient and the other symbols have their usual meaning. The irreversible current-potential-time equation has already been presented (34).

For all potentials from the commencement of the first wave to the diffusion-limited current of the second wave, there would be a significant concentration of Z present during the electrolysis. Up to the potentials where the second electron addition becomes important the formation of Z

would be 100% current efficient.

There would only be a single wave in the current-voltage curve if the second electron addition is driven far to the right at potentials where the first process becomes important. For all four cases there would never be a significant concentration of Z at any potential. The current-voltage curves for systems like (39) and (40) could be described by the equation for totally irreversible polarographic waves (34). For a system such as (37) the current-voltage curve could be described by (41) while the expression for the current-voltage curve for (38) would be complex [37].

If both electron transfer processes become important in the same potential region, at each potential there will be a finite concentration of Z present at the electrode surface. The current efficiency for the formation of Z would at all potentials be less than 100%. Berzins and Delahay [37] have treated rigorously the current-voltage curves for systems (38) and (40). For their derivations they considered semi-infinite linear diffusion as to sole means of mass transport.

In order to carry out calculations of this type, the current must be assumed to be the sum of two components, assumed to be the sum of two components:

$$i_{total} = i_{O/Z} + i_{Z/R}. \qquad (42)$$

The first component is for the O/Z couple, while the second component is for the Z/R couple. The calculation of current for the O/Z couple is relatively straightforward. For the irreversible case it is (34) while the calculation for the reversible case is shown below:

$$i = nFAD_0^{\frac{1}{2}} C_0^o \quad \frac{1}{\pi^{\frac{1}{2}} t^{\frac{1}{2}} (1 + \Theta [D_0/D_R]^{\frac{1}{2}})} , \qquad (43)$$

where $$\Theta = \frac{C_0(0,t)}{C_Z(0,t)} = \frac{f_Z}{f_0} \exp\left[n_1 F(E-E^o)/RT\right] . \qquad (44)$$

The quantities $C_o(0,t)$ and $C_Z(0,t)$ which are functions only of time and potential correspond to the surface concentrations of O and Z. The value of Θ is fixed by the applied potential, E.

The calculation of the contribution to the current for the Z/R couple would be much more complex. When O is reduced to Z, the molecule Z has three possible fates; it could be reduced to R, be re-oxidized to O or it could diffuse away from the electrode. Consideration of the diffusion of Z versus its further reduction is the key of the Berzins and Delahay approach.

For the case of two consecutive irreversible reductions, (40), Berzins and Delahay used a balance for Z at the electrode surface as one of the boundary conditions in the solution of the diffusion problem:

$$C_0^o k_1 \exp(k_1^2 t/D_0) \operatorname{erfc}(k_1 t^{\frac{1}{2}}/D_0^{\frac{1}{2}}) - k_2 C_Z(0,t)$$

$$+ D_Z \left[\partial C_Z(x,t)/\partial x\right]_{x=0} = 0 . \qquad (45)$$

The first term of (45) corresponds to the electrochemical rate of formation of Z at the electrode surface, the second term considers the electrochemical

rate of reduction of Z to R, while the third term considers the rate of diffusion of Z away from the electrode surface. The subscripts 1 and 2 refer to the heterogeneous rate constants for the first and second electrons respectively. The calculated current-potential-time equation is shown below:

$$i = n_1 FAC_0^o k_1 \exp(k_1^2 t/D_0) \operatorname{erfc}(k_1 t^{\frac{1}{2}}/D_0^{\frac{1}{2}}) + \frac{n_2 FAC_0^o k_2}{(D_Z/D_0)^{\frac{1}{2}} - k_2/k_1} \left[\exp(k_2^2 t/D_0) \operatorname{erfc}(k_2 t^{\frac{1}{2}}/D_0^{\frac{1}{2}}) - \exp(k_1^2 t/D_Z) \operatorname{erfc}(k_1 t^{\frac{1}{2}}/D_Z^{\frac{1}{2}}) \right] . \quad (46)$$

It is now possible to calculate the current efficiency for the formation of Z as a function of potential. This can be done by dividing the current for the O/Z couple by the total current as given below.

$$CE_Z = \frac{i_{0/Z}}{i_{0/Z} + i_{Z/R}} \quad (47)$$

For the case of a reversible reduction preceding an irreversible one, (38), Berzins and Delahay again used the concept that the total current is a sum of two components, (42). To solve the boundary value problem, they used as one boundary condition the sum of fluxes of 0, Z, and R at the electrode surface, as given below:

$$D_0 \left[\partial C_0(x,t)/\partial x\right]_{x=0} + D_Z \left[\partial C_Z(x,t)/\partial x\right]_{x=0} - k\, C_Z(0,t) = 0 . \quad (48)$$

The current-potential-time equation is given by the following expression:

$$i = \frac{nFAC_0^o}{\Theta + (D_Z/D_0)^{\frac{1}{2}}} \left[(D_Z/t\pi)^{\frac{1}{2}} \right.$$

$$\left. + \frac{k\left[2\Theta + (D_Z/D_0)^{\frac{1}{2}}\right]}{\Theta + (D_Z/D_0)^{\frac{1}{2}}} \exp(a^2 t)\, \mathrm{erfc}(at^{\frac{1}{2}}) \right] , \qquad (49)$$

where Θ is defined by (44) and (a), as given by

$$a = k/\Theta D_0^{\frac{1}{2}} + D_Z^{\frac{1}{2}} . \qquad (50)$$

By the use of (47) it is possible to calculate a current efficiency for the formation of Z when the proposed mechanism, (38), is a sequential reversible-irreversible process.

IV. EXPERIMENTAL

A. Electron Spin Resonance

A Varian V-4500 spectrometer with 100 kc modulation and a six-inch electromagnet was used for all experiments where electron spin resonance absorption spectra were taken. The microwave cavity was fitted with a modified Varian V-4548 aqueous sample cell. The cell was modified by removal of the T 7/25 joint which was replaced with a T 14/35 male joint.

The display of the spectrometer was a first derivative of the absorption spectrum presented on a Sargent SR recorder which had a one-second pen response.

B. Electrochemistry

1. Electrode design for electrolysis within the microwave cavity of the ESR spectrometer

An electrode was constructed (Figure II) similar in design to the electrode of the Varian V-4556 electrolytic cell. This electrode was employed in connection with a Kelley-Fischer-Jones [39] three-electrode controlled-potential polarograph. The working electrode was made of 54-mesh platinum gauze obtained from J. Bishop and Co., Malvern, Pennsylvania. The gauze was fused to one end of a piece of platinum wire sealed in a 3 mm od soft glass tube which passed through one hole of a 2-hole #2 rubber stopper. The other end of the platinum wire was silver soldered to a copper lead extending the length of the soft glass tube. The copper wire was then connected to the appropriate lead of the polarograph.

The reference electrode was an Ag/AgCl electrode. The silver wire, .020" diameter, was wrapped about the 3 mm o.d. glass tubing which contained the lead to the working electrode. Five or six helical turns of this wire were anodized at low current in a NaCl solution. The Ag/AgCl electrode was positioned as close to the working electrode as possible. The remaining silver wire was insulated from the solution by a coating of glyptal resin. The silver wire passed through the same hold in the rubber stopper on the 3 mm o.d. tubing. Several turns of bare wire were then placed about the glass tube so that the alligator clip of the reference lead of the polarograph could be attached. A leveling bulb was connected through the second hole of the rubber stopper.

The counter-electrode was a piece of platinum foil placed in the 12 mm o.d. glass tubing which acted as a reservoir at the top of the cell. This reservoir was connected to the top of the aqueous sample cell by a section of 3 mm o.d. glass tubing with a T 5/20 glass joint.

When in place in the cell, the resistance measured between any pair of electrodes by Industrial Instruments Model RC Conductivity bridge was less than 20,000 ohms.

The working electrode was plated with gold from an alkaline cyanide bath by the method of Blum and Hodgson [40]. It was then dipped into a pool of mercury. The excess mercury was removed by suction. After each day of use, usually only one electrolysis experiment per day, but after less than 6 to 8 hours of use, the mercury and gold were removed with aqua regia and the electrode replated just prior to the next experiment. From

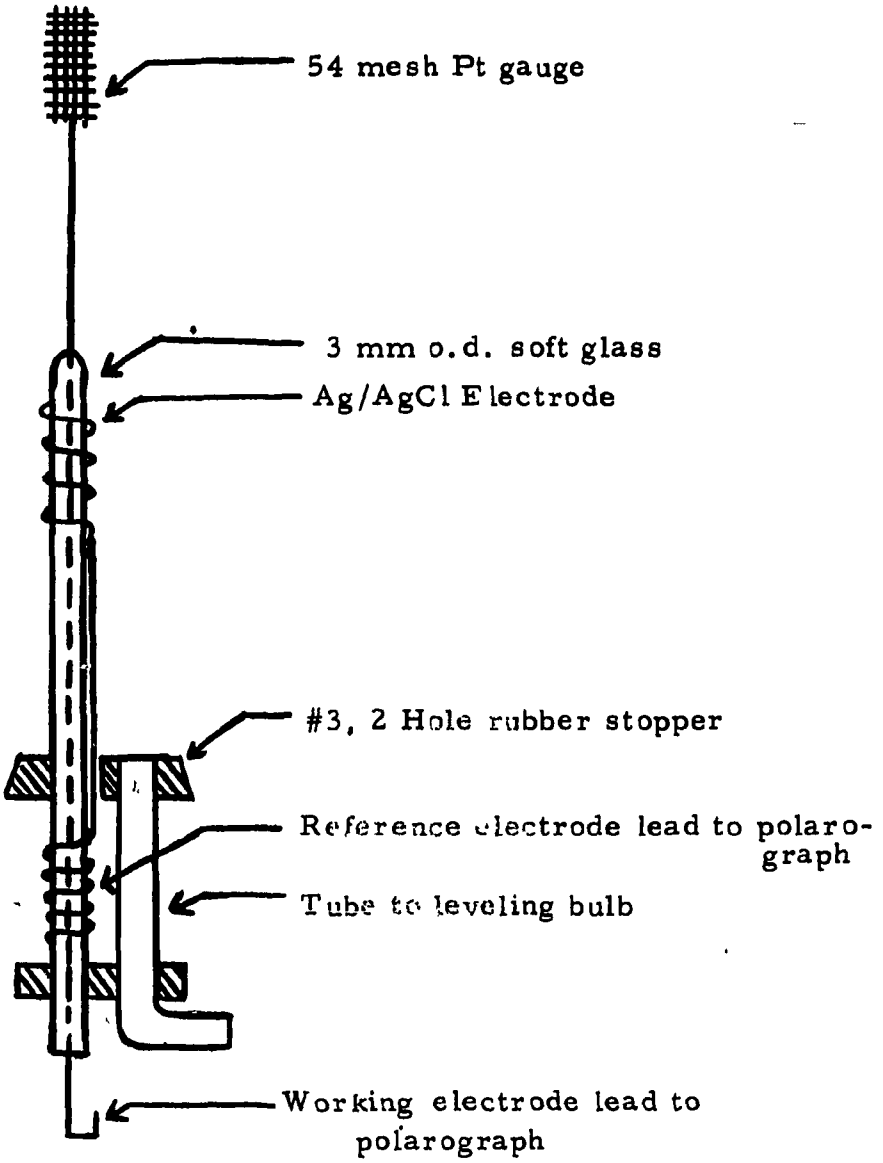


Figure II

Working and Reference Electrode Arrangement. For *in situ* Electrochemical Generation in a Varian Aqueous Sample Cell.

time to time the Ag/AgCl reference electrode was cleaned and replated.

The typical piece of platinum gauze for the working electrode was 3.0 to 3.3 cm long and .3 cm wide, that is, the average electrode was 60 to 65 strands of wire long and 6 to 7 strands of wire wide. For the wire used in 54-mesh gauze, .010 cm in diameter, this size gauze would give a projected area of .40 cm^2 per side.

The rubber stopper holding the reference and working electrodes was inserted into a glass tube with T 14/35 joint. This tube was connected to the aqueous sample cell. The gauze electrode was positioned vertically in the flat portion of the cell such that the tip of the gauze was always slightly above the vertical center of the cell. It was difficult to obtain a reproducible lateral position of the electrode as the electrode tended to fall to the side of the cell. The aqueous cell with electrodes was positioned vertically in the microwave cavity of the spectrometer in such a way that the center of the flat part of the cell was in the center of the microwave cavity. The wave guide and microwave cavity were then placed in their proper position with respect to the pole pieces of the electromagnet.

After the cell, electrode, and microwave cavity were in place, the system was flushed with Linde H.P. dry nitrogen before the electrolysis solution was added. During electrolysis a stream of nitrogen was passed into the previously deaerated solution in the reservoir to prevent oxygen from re-entering the solution.

2. Electrolysis within the microwave cavity of the ESR spectrometer

Two types of electrolysis were carried out within the microwave

cavity. The first was designed to produce a sufficient quantity of radical so that a high-resolution electron spin resonance spectrum could be obtained. The second type of experiment was designed to obtain a relative measure of current efficiency for radical formation as a function of applied potential.

The first type of experiment was carried out in buffered solutions several millimolar in electroactive species while the total concentration on all forms of the buffer was .16 molar. The applied potential was adjusted so that an electron spin resonance absorption signal was observed; the applied potential was then adjusted slightly to maximize the signal without exceeding the current capacity of the polarograph. During the recording of the spectrum an effort was made to keep the current constant by adjusting the applied potential. In the cases of transient radicals the currents were in the range of 100 to 600 microamperes while for stable radicals the currents which were allowed to flow were usually an order of magnitude smaller.

The recording of a high-resolution electron spin resonance spectrum required in most cases 15 minutes, during this time current may have fluctuated as much as $\pm$ 15% in the case of high currents, but less for the smaller currents. In the same time interval the electrode potential for the cases of large currents was made more cathodic by 20 to 40 mv, while for the smaller currents the potential was made more cathodic by less than 20 mv. After each spectrum was recorded, the solution in the cell was agitated to replace both the depleated electroactive species and the buffer. If several high-resolution spectra were recorded without intermediate

agitation, the signal intensity may have fallen for the last relative to the first, but no change in spectrum was detected.

The operational parameters for the spectrometer varied from run to run but a typical set had modulation amplitude 10 or less, klystron power attenuation 4.00 or more and signal intensity level 500 or less. In many cases the modulation was decreased to 6, attenuation increased to 5.00 and signal level decreased to 100. The signal to noise ratio for high-resolution spectra was always better than 20 to 1.

In experiments where relative current efficiencies were measured, the electroactive species was approximately ten millimolar while the total concentration of buffer in all its forms was .16 molar. To obtain the relative current efficiencies the electrode potential was applied and an approximate steady state current measured ($\pm$ 10%). Simultaneous with the current measurement, an electron spin resonance absorption spectrum with large modulation was rapidly recorded. The sweep time was about two minutes. The typical spectrometer settings were modulation, 300 to 800, klystron power altenuation, 4.5, and signal intensity level, 20 to 250. The intensity was measured from peak to base line in millimeters. For many of the potentials, replicate measurements of current and ESR signal were made and these always agreed to better than 20%. If the signal intensity level was changed during a particular series of runs, all intensity measurements were normalized to a common signal level.

3. Observations on radical stability

Experiments similar to those for determination of relative

current efficiency proved useful for determining radical stability. A steady state in both electrolysis current and electron spin resonance signal was obtained. The electrolysis was then discontinued, and the decay of the electron spin resonance signal was followed. For radicals which decayed rapidly, the applied magnetic field was not altered during the decay study. For radicals which decayed slowly the entire spectrum was rapidly scanned several times. For short-lived radicals, a twelve-inch-per-minute chart drive was used on the Sargent SR recorder, but for long-lived or stable radicals a one-inch-per-minute recorder chart drive was employed. Duplicate runs were always made for the radicals which decayed rapidly. The electron spin resonance signal intensity was measured from the base line to the maximum deflection of the second derivative signal.

4. Polarography

Polarograms were run on aliquots of the solutions employed for in situ generation of free radicals. The polarograph employed was the same three-electrode polarograph already described [39]. The reference electrode was an Ag/AgCl electrode and the counter electrode was a saturated calomel electrode. The cell employed was a fifty-milliliter beaker fitted with a rubber stopper. A gas dispersion tube using Linde H.P. dry nitrogen was used to deaerate the solution.

The polarography of nitroferrocene was carried out in a conventional "H-Cell" which had a 10 milliliter sample compartment, sintered glass disk, agar plug, and internal saturated calomel reference electrode S.C.E. This reference electrode was constructed by the method described

by Meites [41]. The sample compartment was wrapped with black electrical tape to exclude light and the polarographic experiments were carried out in a darkened room. The dropping mercury electrode employed was also of a conventional design consisting of a six inch piece of Marine Barometer Tubing obtained from Corning Glass Works. The characteristics of this capillary were determined at 60 cm. head of mercury in 25% v/v $EtOH/H_2O$. At -.50 v vs S.C.E. the drop time, τ, was 4.86 sec/drop, while the mass flow rate of mercury, m, was 1.765 mg/sec; the quantity $m^{2/3}\tau^{1/6}$ at -.50v S.C.E. was calculated to be 1.899.

The polarograph employed for the nitroferrocene studies was a Sargent XV polarograph modified with a "one second" pen drive motor.

5. Solutions

The solutions of the several nitrocompounds investigated were prepared as follows: A known amount of nitrocompound was dissolved in sufficient 95% ethanol so that the final solution would be 50% v/v $EtOH/H_2O$. After the nitrocompound dissolved completely the buffer constituents were added such that the total concentration of all forms of the buffer was .16 molar, while the chloride ion concentration from either KCl or HCl was .10 or .20 M. The concentration of diverse electrolyte, KCl, was in all cases greater than or equal to .10M but less than .20M. Sufficient water was added to insure the desired 50% v/v $EtOH/H_2O$. The ratio of protonated to unprotonated forms of the buffer was in the range of 7/1 to 1/7.

Solutions of nitroferrocene for polarographic investigations were prepared by determinate weighing and subsequent dissolving of nitroferrocene

in 95% EtOH contained in a ruby, anti-actinic volumetric flask. An aliquot of this stock solution was pipetted into a second volumetric flask which already contained the buffer constituents, KCl, and sufficient EtOH such that when diluted to the mark with water, the total concentration of all forms of the buffer was .080M, .20M in KCl and 25% v/v EtOH/H_2O. These solutions were prepared in a darkened room and stored in the dark until used. The experiments were designed such that in most cases, the ratio of protonated to unprotonated form of the buffer varied between 1/4 to 4/1. The water used was singly distilled after it had been deionized. The buffer systems employed were acetic acid-acetate, dihydrogenphosphate-monohydrogenphosphate and "Tris".

In experiments which were designed to compare the polarographic behavior of ferrocene and nitroferrocene, nitrate replaced chloride as the anion of the diverse electrolyte and the solutions were 50% v/v EtOH/H_2O.

Solutions of ferrocene for polarographic investigations were prepared in a manner similar to those for nitroferrocene except that the supporting electrolyte contained no added chloride ion and that the solvent was 50% v/v EtOH/H_2O. No buffer was employed since no protons are involved in the electrochemical oxidation.

All pH measurements were made using the micro electrodes of a Model G Beckman pH meter. These electrodes were standardized against the appropriate aqueous reference buffer solution obtained from Leeds and Northrup Co. The balance employed was a Mettler type H-16 single pan balance.

6. Reagents

All chemicals used in this study were reagent grade meeting ACS specifications except those listed below.

D_2O was batch XIX 99.5% D_2O obtained from General Dynamics Corporation, Liquid Carbonic Division, 767 Industrial Road, San Carlos, California.

4,4'-dipyridyl dihydrochloride was obtained from Aldrich Chemical Co., Inc., 2369 N. 29th St., Milwaukee 10, Wisconsin.

1,1-diphenyl-2-picrylhydrozyl, DPPH, was obtained from the Aldrich Chemical Co., Inc.

N,N'-dimethyl-4,4'-dipyridyl (methyl viologen) was lot 297895 obtained from K & K Laboratories, Inc., 177-10 93rd Ave., Jamaica 33, New York.

The several nitrocompounds were all Eastman "White Label" obtained from Eastman Chemical Co. and used without further purification. They were: 1-chloro-4-nitrobenzene, 1-chloro-3-nitrobenzene, para-nitrobenzoic acid and para-nitroanisole.

N-methylpyridynium iodide was prepared by the method of Prescott [42]. The melting point of the twice- recrystalized product was 116.5-117°C, while the literature value is 117°C.

Nitroferrocene was kindly provided by Dr. K. L. Rinehart of these laboratories. It was prepared by the method of Grubert and Rinehart [43]. The recrystallized product provided was chromatographed according to the following procedure: a .5 gram sample of nitroferrocene

was dissolved in 200 ml of 3:1 v/v benzene/pentane and added slowly to a 2 x 26 cm. column containing 96 g Merck Neutral Wash Alumina. The adsorbed nitroferrocene was eluted with additional mixed solvent. The leading and trailing edges of the band were discarded and only the center portion was retained. The solvent was removed slowly at room temperature under vacuum. The melting point of the resulting red crystals was 128.0-128.5°C. The melting point when recrystalized from cyclohexane is reported to be 130°C [43]. Analysis yielded: C, 52.43; N, 6.03; H, 3.99. Theoretical values for $C_{10}H_9O_2NFe$ are C, 51.99; N, 6.06; H, 3.93.

Ferrocene was obtained from the Ethyl Corporation and used without further purification.

Sodium 1-nitrocyclopentadieneide was kindly provided by Dr. K. L. Rinehart of these laboratories. It was prepared by the method of Thiele [44].

2-Amino-2-(hydroxymethyl)-1,3-propanediol was Eastman technical Grade #T-370 used without further purification. This reagent has the common names of "Tris" or "Tam", and is used as a buffer with a pKa = 8.3.

The mercury used was purified by aeration while under dilute nitric acid. After pinholing the mercury was distilled once under vacuum.

7. Coulometry at a mercury macro-electrode

The electrolysis vessel used in these studies was a 200 ml electrolysis beaker. The electrode arrangement was similar to that shown by Lingane [45] except the counter electrode was an SCE. Polarograms of the catholyte were recorded at intervals during the electrolysis using a

Sargent XV polarograph. Linde H.P. dry nitrogen which had been passed through a gas wash bottle containing V(II) was used to purge the system of dissolved oxygen. A Sargent Coulometric Current Source, Model IV, (E. H. Sargent and Co., Chicago, Ill.) was employed as the constant current source. Vigerous stirring was provided by an overhead Bodine Motor Model 102 manufactured by Tolboys Instrument Corp., Emerson, N.J.

Currents of 9.65 ma were passed; with an electrode area of 20 cm^2, the current density was therefore .5 ma/cm^2.

The catholyte volume was 120 ml. This solution was .02 M $NaClO_4$ and .04 M NaOH and contained 2.01 millimoles of N-methylpyridinium Iodide. The concentration of reducible species was therefore 16.7 millimolar. The electrolysis was carried less than 35% to completion to insure that complete concentration polarization of N methylpyridinium ion was not achieved.

V. RESULTS AND DISCUSSION

A. Electrode Design and Electrochemical Measurements in the ESR Spectrometer

The advantage of the cell used in this study over those described previously in the literature is that a large mercury surface is available to perform the electrolysis. The cell described by Maki and Geski [46] was a 3 mm . . tube with a mercury micro-pool at its base. Such a cell is limited in electrode surface area, $\sim$.025 cm.^{2} The amalgamated gauze used in these experiments had a working area of $\sim$1 cm.^{2} The pool electrode is also undesirable because the resistance of the solution between the reference and working electrode becomes appreciable in cells of such restricted dimensions. Piette, Ludwig and Adams [15] have recently described the use of the Varian aqueous sample cell half filled with mercury. This electrode arrangement is also restricted in surface area and high in resistance. The cell used in the present studies had less than 20,000 ohms reference to cathode resistance which is an improvement but still significant.

The polarograph [39] employed in this study is far superior to the conventional two electrode polarograph when performing electrochemical experiments in systems with high resistance. The virtue of the three-electrode system is that a potential can be imposed between the working electrode and the reference electrode while the current is drawn between the working electrode and the counter electrode. The major advantage is that the cathode potential with respect to the reference is directly controlled rather than depending upon total cell emf as in the two-electrode systems. The three-electrode system employed here has a further advantage in that

the potential control circuit and current measurement circuit are independent. The electrode geometry employed in these studies has an advantage in that the reference electrode is not interposed between the working cathode and the counter anode, but rather is located behind the working cathode; thus, the reference electrode is out of the field of the cathode and counter electrodes.

The applied potential can then be related to potentials applied in systems where "iR" drop is unimportant. A comparison of ESR-potential data to conventional polarographic data is now possible this is a property not available in the earlier studies.

B. Calibration of the ESR Spectrometer

Of the two methods proposed by Ingram [33] to calibrate an ESR spectrometer, a relative calibration using a sample with a known number of spins is the most convenient.

The spectrometer used in these experiments was calibrated in two ways. The first was the relative calibration technique suggested by Ingram using 1,1-diphenyl-2-picrylhydrozyl, DPPH. Benzene solutions of DPPH were prepared determinately from the solid. ESR spectra of 1×10^{-4}, 2.5×10^{-5} and 1×10^{-5} M solutions were recorded under the following instrumental conditions: modulation of 100, klystron power attenuation of 4.50 and signal intensity levels of 200 (400 for the 10^{-5}M solution). The aqueous sample cell with the gauze electrode was used. Under these conditions the spectrum is reduced to 5 lines and measurements were made at the maximum of the center derivative peak. The signal to noise ratio

under these conditions is 35:1 for 1×10^{-4} M, 10:1 for 2.5×10^{-5} M and 4:1 for 1×10^{-5} M DPPH. These spectra were not doubly integrated as suggested by Ingram but rather they were used as a qualitative guide to the number of spins that could be detected with a given signal to noise ratio. Since the DPPH radicals were uniformly distributed throughout the cavity rather than localized in the vicinity of the gauze electrode as were the electrochemically generated radicals, this type of calibration can only be qualitative in nature. The problem of uniform versus non-uniform radical distribution is important because the sensitivity of the spectrometer's detection system is a maximum at the vertical center of the cell and falls nonlinearly to zero at the top and bottom of the cell.

The second calibration procedure employed was an electrochemical generation of meta-chloronitrobenzene anion radical in acetonitrile. The advantage of this second calibration procedure is that the radical is generated in the same manner and position as in the electrochemical experiments. A given number of coulombs was passed and the ESR signal measured under conditions used for the relative efficiency and relative intensity studies. It was assumed that the $ArNO_2^-$ radical was generated with 100% current efficiency. Such an assumption seems warranted when acetonitrile is the solvent based on electrochemical and ESR experiments of Maki and Geski [13, 46]. Electrolysis current was passed for about 4 seconds to generate meta-chloronitrobenzene anion radical. ESR spectra were recorded during generation and for times after generation until the ESR signal was indistinguishable from background. The radicals were observed

to decay with a half-life of 18 seconds for at least 4 half-lives. This time is comparable to the half-life observed for the disappearance of these radicals in the aqueous experiments.

In various experiments the quantity of electricity passed was sufficient to generate from $.8 \times 10^{14}$ to 10×10^{14} radicals if the process was 100% current efficient. The chart displacement from the base line extrapolated to zero time was 170 mm for 8.3×10^{14} radicals, 70 mm for 5.8×10^{14} radicals, 65 mm for 5.0×10^{14} radicals and 35 mm for 2.2×10^{14} radicals. The average was 6.8×10^{14} radicals per 100 mm of chart displacement. The noise level was 1 mm on either side of zero. The spectrometer settings were modulation, 800, signal level, 160, and attenuation, 4.50. Under these conditions the spectrum is reduced to 8 lines and measurements were made at the maximum deflection of the derivative spectrum.

Although the site of radical formation is the same in the aqueous and non-aqueous experiments, the radical concentration profile within the cell is not the same because of different electrolysis times. The uniform distribution in the DPPH case versus the extreme localization of the electrochemically generated radicals are the two extremes of possible concentration profiles. An upper and lower limit of radical concentration can be made by using estimates based on both the uniform and the localized concentration profiles. Under spectrometer modulations employed the several spectra recorded were not single line spectra. Under these conditions different hyperfine structure will be "added together" by the modulation in different ways; thus, the deflection of the derivative spectrum

observed will only be a qualitative guide to compair the number of unpaired spins present for two different radicals. These estimates are designed to give order of magnitude estimates, so that in later experiments the question whether radicals play a major or minor role in the electrochemical mechanisms can be resolved.

C. Aromatic Nitrocompounds

1. Analysis of spectra

ESR spectra are observed during the electrolysis of both meta- and para- chloronitrobenzene, (Figure III), para-nitroanisole, and para-nitrobenzoic acid, (Figure IV). For the case of meta-chloronitrobenzene the same radical is observed in acetate buffers and unbuffered solution, but no radicals are observed in .05 and .10M strong acid. para-Chloronitrobenzene and para-nitroanisole radicals are observed in acetate buffer, but not in strong acid. The same radical of para-nitrobenzoic acid is observed both in acetate and "tris" buffer solutions.

The spectra of all nitrocompounds possessed an obvious three-fold symmetry with an intensity ratio of 1:1:1. This major splitting is ascribed to the nitrogen which has a nuclear spin of 1. Each of the 3 multiplets of the para-substituted compounds consists of nine lines. These splittings are ascribed to the two sets of two equivalent ortho and meta ring protons which have a nuclear spin of 1/2. The assignment of a particular coupling constant to a particular set of protons cannot be done without unambiguous substitution of deuterons for one set of protons. The ESR spectra of

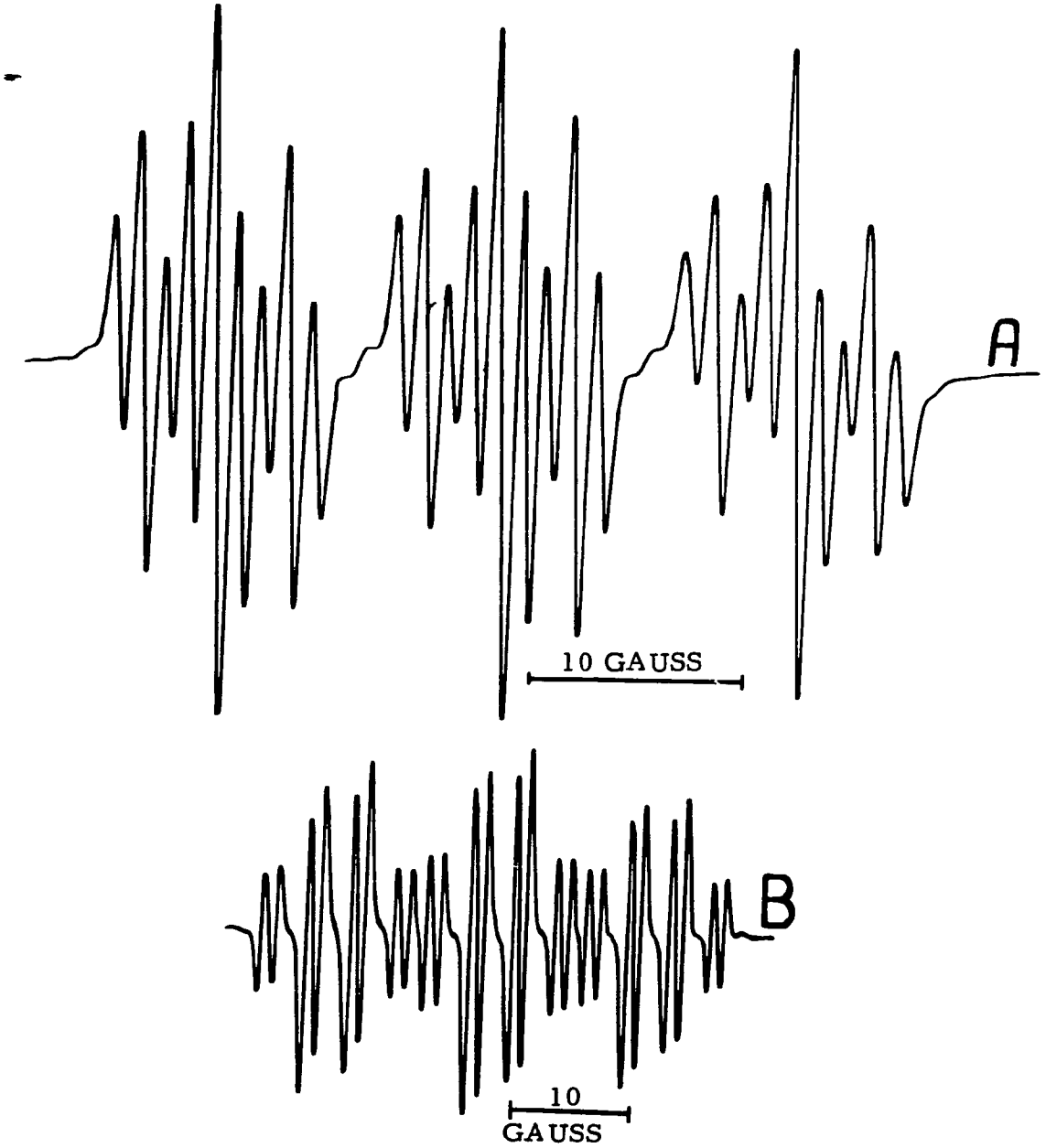
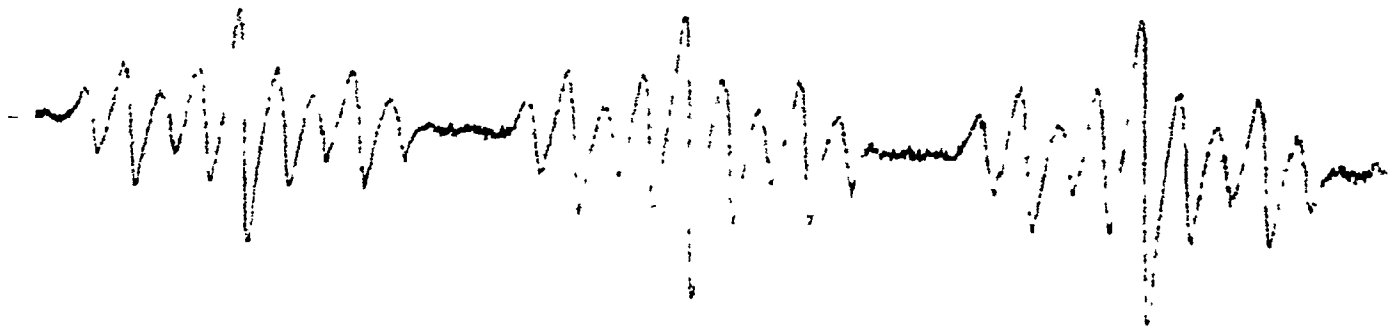
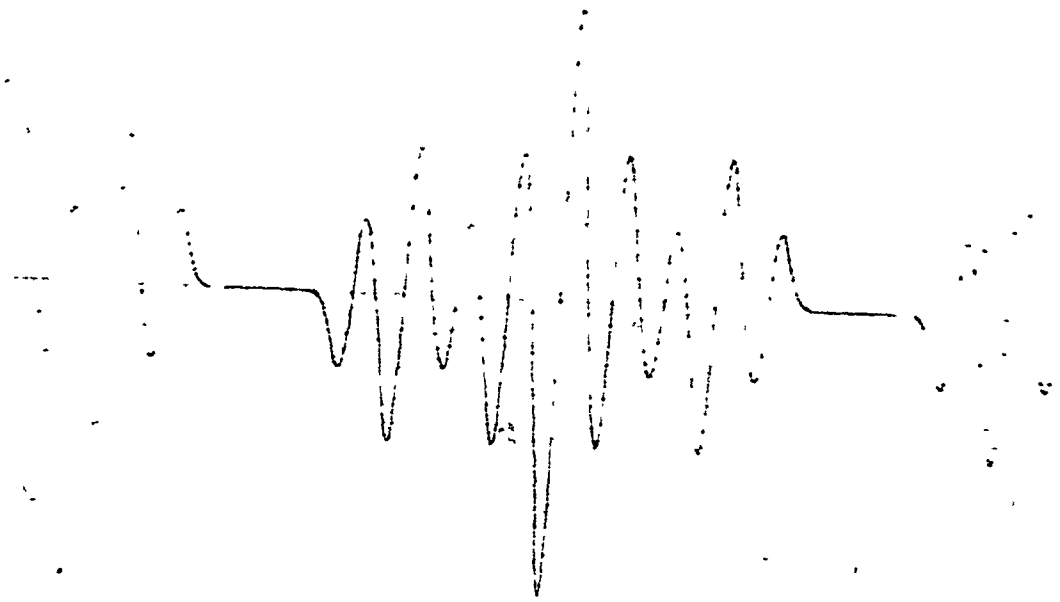


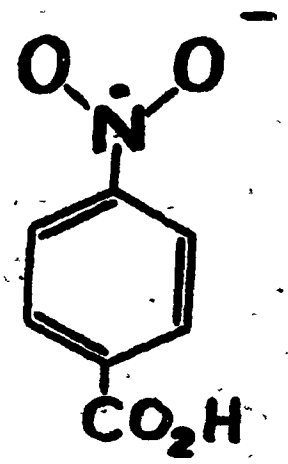
Figure III. ESR Spectra of para-chloronitrobenzene (A) and meta-chloronitrobenzene (B).



$a_N = 12.8$
$a_{H_o} = -3.3$
$a_{H_m} = 1.1$

ESR Spectrum of para-nitrobenzoic acid electrochemically generated





ESR Spectrum calculated using computer program (see text).

Figure IV

meta-chloronitrobenzene may be interpreted as arising from three equivalent or nearly equivalent ring protons, and a fourth proton with a significantly different splitting constant. The determination as to which three of the four ring protons are equivalent again can only be achieved by substitution of deuterons for protons. Substitution of chlorine atoms for protons in the case of semiquinones [47] does not appreciably alter the spin density of the unpaired electron and therefore does not appreciably alter the splitting constants. For this reason since both of the splitting constants of meta-chloronitrobenzene are approximately equal to those of para-chloronitrobenzene, the three equivalent protons are believed to be those protons ortho and para to the nitrogroup. The smallest coupling constant a_{H2} is therefore assigned to the single proton meta to the nitrogroup.

Table I is a compilation of observed coupling constants. Several of the compounds were also observed to give radicals in acetonitrile [13], their coupling constants are also included in the table.

Piette, Ludwig and Adams [14] have reported that the magnitude of the nitrogen coupling constant in water is 3 to 4 gauss larger than for the radicals from the same substituted nitrocompound when generated in acetonitrile. This difference is also observed in the present study. Such differences in nitrogen coupling constants could result from some solvent interaction with the nitrogroup manifesting itself as a change of the O-N-O bond angle and/or the angle of the O-N-O plane relative to the plane of the ring. Other possible explanations could be that this radical observed in water results from a three-electron reduction of the nitrocompound,

Table I

ESR Coupling Constant in Gauss for Several Nitroaromatic Free Radicals

Compound	Solvent	a_N	a_{H_1}	a_{H_2}	a_{H_3}
para-chloronitrobenzene	50% EtOH/H_2O	13.08	3.41 (a)	1.04 (a)	
para-chloronitrobenzene	acetonitrile	9.83	3.46 (a)	1.17 (a)	
para-nitroanisole	50% EtOH/H_2O	14.35	3.52 (a)	1.10 (a)	.3 (b)
para-nitroanisole	Acetonitrile	11.57	3.43 (a)	1.11 (a)	.30 (b)
meta-chloronitrobenzene	50% Et OH/H_2O	12.91	3.46 (b)	1.05 (c)	
para-nitrobenzoic acid	50% EtOH/H_2O (pH=4)	12.80	3.31 (a)	1.10 (a)	

(a), 2 equivalent spins of 1/2

(b), 3 equivalent spins of 1/2

(c), 1 spin of 1/2.

or that the radical observed is the protonated form of the one-electron reduced species, $ArNO_2H$ (vida infra).

2. In situ electrochemical studies and the electrochemical mechanism

A radical spectrum of meta-chloronitrobenzene, I, is not observed in strong acid. A radical is observed in 7:1 $HOAc/OAc^-$ buffer and in unbuffered solution, but the spectrum is exceedingly weak. In 1:1 and 1:7 $HOAc/OAc^-$ buffers the spectra observed are very intense.

Figure V is a polarogram of meta-chloronitrobenzene in 1:1 $HOAc/OAc^-$ buffer. Plotted on the same potential scale is the relative efficiency for radical formation. The relative efficiency was evaluated by dividing the steady state maximum chart displacement of the ESR spectra by the steady state electrolysis current. It can be seen that even at the polarographic half wave potential there is still a detectable quantity of radical present.

Using the DPPH method of calibration the steady state number of spins present is 1×10^{16}. This estimate was obtained by comparing the DPPH signal to noise ratio to the 70:1 signal to noise ratio of meta-chloronitrobenzene radical at -.400 v versus Ag/AgCl ($M/10\ Cl^-$). The estimate of the number of radicals using electrochemical generation as the means of calibration is 2×10^{15} unpaired spins. The disparity in total spins is probably due to three factors: the first is the obvious difference in concentration profile, the second is difference in spectrum shape and the third and less likely is that the reduction of nitrocompounds in acetonitrile is not 100% current efficient (vida supra).

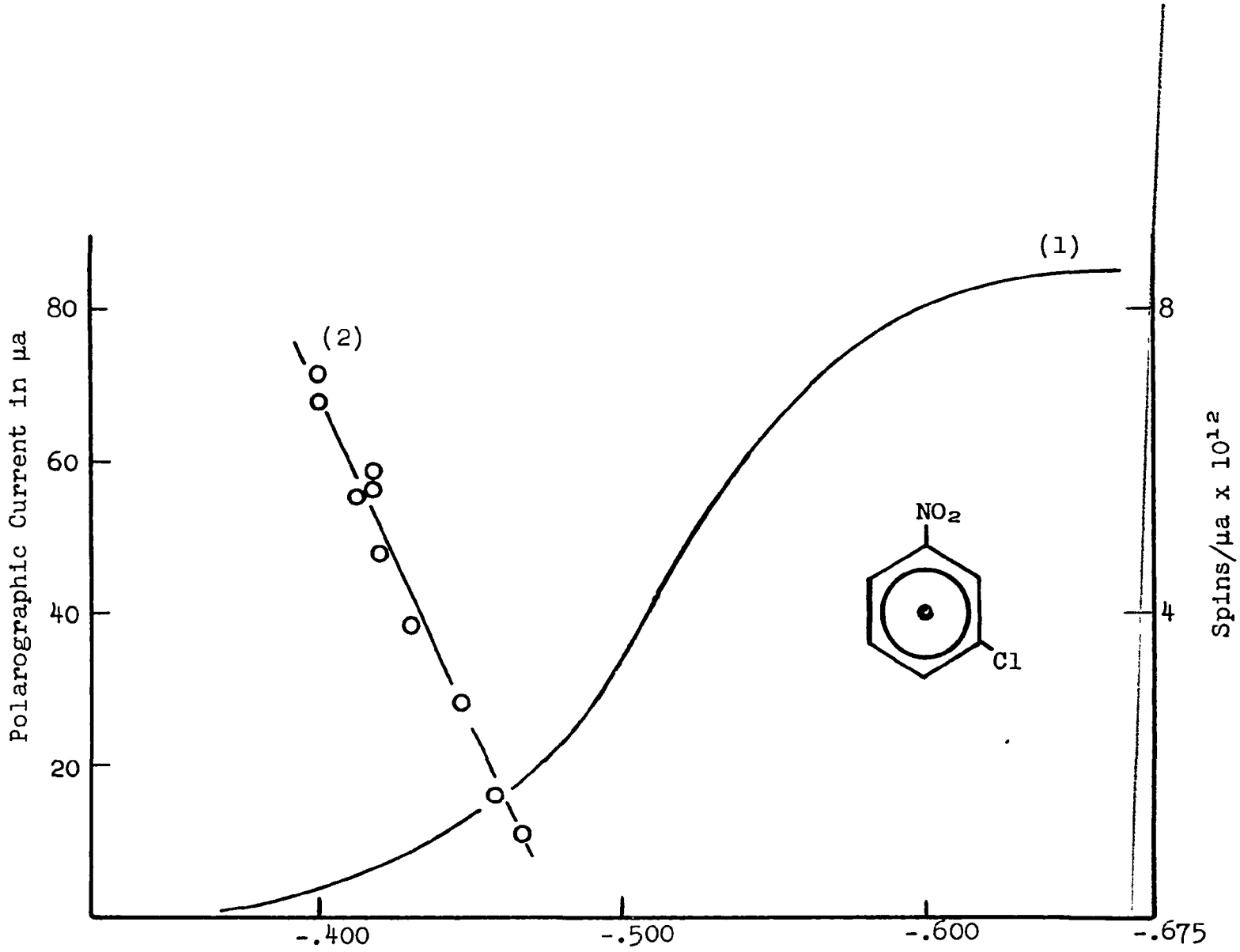


Figure V.

Polarogram of meta-chloronitrobenzene (1) in μa on the same potential axis as relative efficiency for radical formation (2) in units of steady state spins per μa of electrolysis current in 1:1 HOAC/OAc^- buffer 50% v/v EtOH/H_2O.

The radicals of meta-chloronitrobenzene and para-nitrobenzoic acid in water are observed to decay when the electrolysis is discontinued. Both radicals decay by first order kinetics with a half-life of 24 seconds until the ESR signal becomes indistinguishable from background. This decay time is too short to be due to diffusion either out of the cell or from a region of high detection sensitivity to a region of low detection sensitivity. It has been shown [48] that for a planar electrode when the diffusing species is concentrated at the electrode surface at t = 0 that after time (t), the average value of the square of the distance from the electrode (when $x > 0$) is that given below.

$$\langle x^2 \rangle = 2\ Dt\ . \tag{51}$$

The root-mean-square distance traveled from the electrode surface after 48 seconds (2 half-lives) assuming a D of 1×10^{-5} cm^2 sec^{-1} is 3.1×10^{-2} cm. This should be an upper limit on the root-mean-square displacement occurring during the same time interval in the decay studies discussed above. Since electrochemical generation has been underway for at least several minutes, a concentration gradient of free radical about the electrode has been established. Under conditions of an already established concentration gradient the average value of the displacement of radicals generated for a given time interval could be no greater than if there were no established concentration gradient. Differences in spectrometer sensitivity with vertical displacement of even 10×10^{-2} cm are not greater than 10%.

The concentration profile established during the electrolysis resembles that of a planar electrode at distances removed from the periphery

of the gauze electrode. In the volume elements between the several strands of wire making up the electrode the concentration profile should be quite constant with respect to diffusion after the electrolysis is discontinued. For the above reasons it is felt that diffusion is not the major cause of the decrease in signal. Convective mass transport probably occurs in this cell. Since convection in this cell comes about only from density gradients, and since little density change should occur because during the electrolysis no material is removed from solution, and since current voltage curves on the gauze electrode are well behaved, any convection that does take place must at most only be comparable to diffusion.

The disappearance of radical must be chemical in nature. It is therefore proposed that the path for the disappearance of radical after discontinuance of electrolysis is a redox reaction with some constituent in large excess, probably the solvent.

Piette, Ludwig and Adams [15] have recently reported observing ESR spectra of several electrochemically generated radicals of nitroaromatics in aqueous solution. They state that the half-lives for decay of these radicals in basic solution, pH 7-8 is 5 to 10 seconds. They attribute this decrease in ESR signal to diffusion of the radical completely out of the electrolysis cell which was a Varian aqueous sample cell half filled with mercury. Based on the calculation discussed above (51) such a decay in even 4 half-lives (40 sec.) could not be due to a significant diffusion of the radical over a 4 cm path needed to escape from the cell. The decrease in signal strength in their case as in the case discussed above must be due to a homogeneous chemical reaction.

The radical which is observed in water must be identified in order to draw any conclusions about the mechanism which is operating. Of the several conceivable radicals which could give rise to the spectrum the least probable is the three-electron reduced state because such a charge type is unlikely in solution. This objection becomes less serious if, in order to reduce the charge, several protons are added along with the three electrons. Proton splittings in the ESR spectrum other than that number expected from the several ring protons are not observed. That the added protons should rapidly exchange with the environment so that their splittings are not observed (vida infra) is difficult to rationalize.

The radical which is observed could result from a protonated one-electron radical. This species, $ArNO_2H$, should have a spectrum which differs from $ArNO_2^-$ in both the number of lines and coupling constants. Spectra of $ArNO_2^-$ have already been reported [13]. The protonated species has an odd number of spins and therefore should have no line in the center of the spectrum; however, the observed spectrum does have a line in the center. If the proton of $ArNO_2H$ exchanged rapidly with its environment, an upper limit of the lifetime of the protonated form can be set using the uncertainty principle.

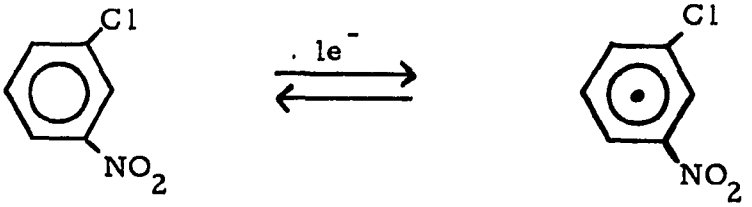
$$\Delta\tau \approx \frac{h}{4\pi\beta\Delta H} \quad . \tag{52}$$

If the coupling constant, H, for the proton is just the magnitude of the observed line width, .12 gauss, then $\Delta\tau$ would be 2.3×10^{-7} sec. If the coupling constant is larger than .12 gauss, $\Delta\tau$ would only be smaller.

Since the same radical for p nitrobenzoic acid is observed in pH 7 buffer as in pH 4.0 buffer and since the same radical of m-chloronitrobenzene is observed in pH 4 buffers and unbuffered solution (at the electrode surface pH$\sim$10), the species $ArNO_2H$ must either be an exceedingly weak acid which exchanges its proton rapidly with the environment or the species $ArNO_2H$ is not the entity causing the observed spectrum.

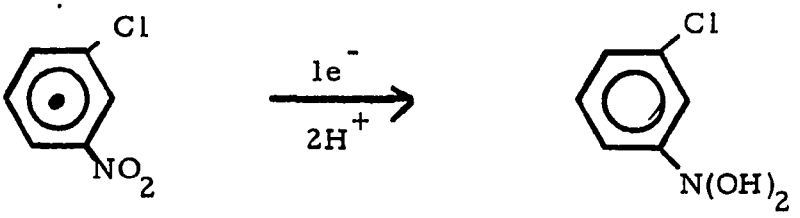
Piette, Ludwig and Adams [15] have attributed the observed spectrum to the anion radical of the parent nitrocompound. Such an assignment seems warranted in view of the similarity of coupling constants for radicals resulting from the same compound in both acetonitrile and water, Table I. The observed difference in coupling constants in the two solvents is believed to result from a solvation effect which causes either a change in the O-N-O bond angle or the angle of the O-N-O plane relative to the plane of the ring.

Since the one-electron radical of an aromatic nitrocompound is observed and is relatively stable in water, the electrochemical mechanism consistent with these observations is a set of sequential one-electron steps which procede at comparable rates. The first electron is probably added reversibly as shown by cyclic voltammetry [12, 15] and the reversible one-electron reductions in acetonitrile [13]. A mechanism consistent with the ESR data presented here and electrochemical data presented elsewhere [9] is that shown below:

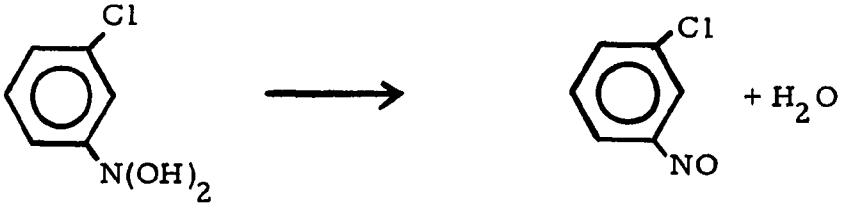


(53)

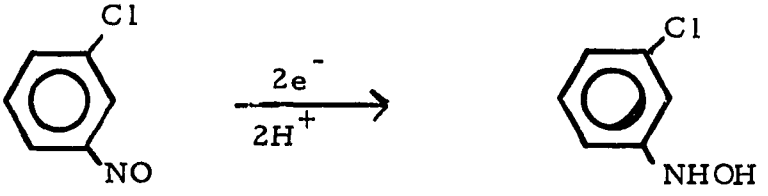
I



(54)



(5)



(6)

The importance of a one-electron reduced intermediate in the electrochemical reduction of aromatic nitrocompounds can be determined by evaluating the efficiency for the escape of the radical from the electrode surface. In the experiments where the steady state number of free radicals

which have escaped from the surface was determined, the rate of escape of the electrochemically generated radical, R_{escape}, must be equal to the rate of bulk disappearance via the homeogeneous reaction discussed above, $R_{B.D.}$:

$$R_{escape} = R_{B.D.} \tag{55}$$

where $$R_{B.D.} = k\,(ArNO_2^-)\,, \tag{56}$$

The value of k from the first-order decay of the ESR signal evaluated when electrolysis is discontinued is .0289 sec^{-1} $spins^{-1}$. The steady state number of spins at each potential multiplied by the rate constant k equals the rate of escape of free radicals from the surface of the electrode. The steady state number of spins as shown in table II was evaluated using the electrochemical method of calibration.

If the one-electron reduced state was further reduced rather than diffusing away, the observed steady state current at each potential would be larger by the quantity i_{lost} if the 3rd and 4th electron are added rapidly compared to the 2nd electron.

$$i_{lost} = R_{escape}\,(\frac{3F}{N}). \tag{57}$$

In (57) F is the faraday, N is Avagadros number, and 3 is the number of additional electrons necessary to reduce the observed radical to the phenylhydroxylammonium ion.

Table II

Importance of the Anion Radical of meta-chloronitrobenzene as a Function of Potential in 1·1 $HOAc/OAc^-$ Buffer and 50% v/v $EtOH/H_2O$ Solutions

E vs Ag/Ag Cl ($M/10\ Cl^-$)	i_{obs} in μa	Steady State Number of Spins x 10^{-15}	i_{Lost} in μa	$i_{o/z}$ in μa	$i_{Z/R}$ in μa	$\frac{3\, i_{o/z} - i_{Z/R}}{4\, i_{o/z}}$
-.400	600	4.37	96	174	426	13.8
-.400	300	2.03	28	82	218	8.5
-.413	345	1.88	26	93	252	7.0
-.418	485	2.80	39	131	354	7.4
-.418	485	2.73	38	131	354	7.3
-.420	210	.98	14	56	154	6.2
-.430	575	2.18	30	151	445	5.0
-.448	550	1.56	22	143	428	3.8
-.458	525	.86	12	134	391	2.2
-.468	575	.63	9	146	329	1.5

In the notation of Berzins and Delahay [37] the observed current, i_{total}, is the sum of $i_{0/Z}$ and $i_{Z/R}$ where Z is the free radical and R is phenylhydroxylammonium ion. For nitrocompounds the difference between $3i_{0/Z}$ and $i_{Z/R}$ is i_{lost}. This is true because if all the Z which was formed from 0 did not diffuse, $i_{Z/R}$ would be $3i_{0/Z}$, but since some Z is observed to escape from the surface not all the Z is reduced to R, therefore $3i_{0/Z}$ will be greater than $i_{Z/R}$. It is now possible to solve for $i_{0/Z}$ and $i_{Z/R}$ by using the two current equations below:

$$i_{total} = i_{0/Z} + i_{Z/R}, \tag{58}$$

and

$$i_{lost} = 3i_{0/Z} - i_{Z/R}. \tag{59}$$

Calculated values of $i_{0/Z}$ and $i_{Z/R}$ as a function of potential are shown in table II.

The last column in table II is a measure of the fraction of the theoretical total current, $4i_{0/Z}$, which is lost due to diffusion of Z away from the electrode surface. The experimentally observed current is almost 10% less than the theoretical current. This indicates that the free radical is indeed important in the electrochemical reduction scheme.

If the number of spins present at the steady state had been estimated using the DPPH calibration procedure, the importance of the free radical would have been greater.

D. Nitroferrocene

1. The electrochemistry of aromatic nitrocompounds

The chemical literature contains numerous citations to studies of the electrochemistry of aromatic nitrocompounds. The effects of pH and substitution on the descriptive polarography has been reviewed by Kolthoff and Lingane [49]. More recently Clark [9] has reviewed and re-examined the mechanism of the electrochemical reduction of aromatic nitrocompounds. These reductions can be divided into two general groups; virtually all nitroaromatics fall into the first class while only ortho- and para-nitrophenol and para-nitroaniline fall into the second class [49].

The most anodic reduction for the first type corresponds to a diffusion controlled, four electron pH dependent process yielding the corresponding phenylhydroxylamine or phenylhydroxylammonium ion [49]. This polarographic wave is observed to shift 50 to 75 mv/pH unit depending both on the pH range and type of ring substitution. This first cathodic process, in acidic solution only, is followed at more cathodic potentials by a second two electron reduction to the corresponding ammonium ion. Clark [9] has recently described several electrochemical and chemical complications which take place during the initial four-electron reduction.

The second class of nitrocompounds exhibits a single polarographic wave in neutral or alkaline solution corresponding to the six-electron reduction to the corresponding amine. Testa and Reinmuth [50] have recently re-investigated ortho-nitrophenol and have shown that this six-electron process is in reality two successive electrochemical reductions of four

and two electrons respectively. Interposed between these two electrochemical processes is a pseudo first order chemical reaction. This interposed chemical step presumably is the relatively slow elimination of a water molecule. The quinoid product resulting from water elimination is reduced immediately in a second, two-electron process.

2. The electrochemistry of aliphatic nitrocompounds

Aliphatic nitrocompounds can be reduced electrochemically [51, 52, 53]. The product of the first reduction process in buffered solutions of pH < 6 is the corresponding hydroxylamine or hydroxylammonium ion. The second reduction process in this acidic pH region is believed to be the two-electron reduction to the amine or ammonium ion; thus paralleling the behavior of the first class of aromatic nitrocompounds. The chief difference between aliphatic and aromatic nitrocompounds is that the half-wave potential of nitroaliphatics in this pH range is pH independent. At pH > 6 the diffusion limited current is a function of time and decreases to a diffusion limited steady state current, the value of which is dependent on pH and the length of the carbon chain. This cathodic process in alkaline solution is still believed to be the four electron reduction to the corresponding hydroxylamine. The polarography in basic buffers is complicated by a slow bulk chemical transformation of the reducible nitro form to the non-reducible acid form. For certain nitroaliphatics it is possible that the anion form of the nitrocompound may also be an important species in equilibrium.

3. Chemistry and electrochemistry of ferrocene and its derivatives

Numerous chemical investigations have been concerned with the aromatic character of ferrocene (dicyclopentadienyl iron II). These studies have been reviewed by Pauson [54], Rausch, Vogel and Rosenberg [55], and also by Schlogl [56]. Recently Rausch, Fischer and Grubert [57] have compared the aromatic reactivity of ferrocene to the dicyclopentadienyl derivatives of Ruthenium and Osmium.

It has been shown that ferrocene can undergo typical aromatic reactions such as Friedel-Crafts acylation and alkylation, it can be sulfonated, arylated with diazonium salts and metallated with n-butyl lithium. On the other hand, typical aromatic reactions such as nitration have lead to destruction of the molecule, presumably through oxidation of the iron atom [43, 57].

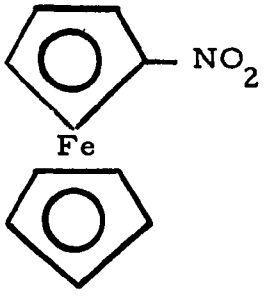
The preparation of nitroferrocene was reported almost simultaneously by Helling and Shechter [58] and by Grubert and Rinehart [43]. The methods of preparation are most unusual for a compound which undergoes the above typical aromatic reactions. The compound can be prepared [43] by treatment of ferrocenyllithium with n-propyl nitrate at -70°C. The structure was confirmed by elemental analysis, conversion to aminoferrocene with iron and hydrochloric acid, and the presence of an infrared absorption at 1507 cm^{-1} typical of aromatic nitrogroups.

Ferrocene can be oxidized chemically to ferrocinium ion by concentrated nitric acid. It has also been oxidized electrochemically in water [59], 90% ethanol [60] and acetonitrile [61]. The electrochemical oxidation in these solvents has been shown to be a reversible one-electron oxidation to ferrocinium ion.

A number of derivatives of ferrocene have been electrochemically oxidized at platinum electrodes [59, 61 to 65] and reduced at mercury electrodes [59, 64, 65]. The oxidation is always of the iron from a formal oxidation state of II to III. The potentials of these oxidations follow the predicted Hammett substituent effect. The electrochemical reduction is always of some ring substituent. These substituted ferrocenes exhibit polarographic behavior similar to the corresponding benzenoid compounds, but the potentials are always more cathodic [59]. The electrochemistry of nitroferrocene has not previously been reported.

4. Electrochemistry and the electrochemical mechanism

A buffered solution of nitroferrocene, Cp_2NO_2Fe, X, at 25° C,



X

which is 25% ethanol by volume, shows one well defined diffusion-controlled polarographic reduction wave in the region of +.4 to -2v versus SCE. The limiting current is proportional to the square root of the height of the mercury column with a zero intercept [66]. No oxidation waves are observed at a dropping mercury electrode up to +.4v versus SCE.

If polarograms of a freshly prepared solution of nitroferrocene are obtained as a function of time, it is observed that the current of the initial polarographic wave decreases rapidly with time, while a second more

cathodic process appears and its current grows with time. Polarograms of a solution of nitroferrocene prepared and stored in a darkened room show no change in diffusion current for several hours.

Figure VI shows polarographic waves for a solution of nitroferrocene kept in a "darkened room" and exposed periodically and reproducibly to an incandescent bulb. It can be seen that with each exposure the first wave decreases while the second wave increases. In the interim between exposures no change in wave character is observed. Figure VII is a plot of polarographic current versus exposure time for the first wave, the first wave plus the second wave, and for the second wave alone. It can be seen that the change in current is linear with exposure time. The limiting current for the growing cathodic wave is also a diffusion-controlled process.

The possibility of a rapid homogeneous chemical decomposition was precluded by comparing the current-time behavior of a nitroferrocene solutions kept at $0^{\circ}C$ and $25^{\circ}C$ in a lighted room. The rate of change of current with time is just as rapid at $0^{\circ}C$ as it is at $25^{\circ}C$.

In a pH 6.47 phosphate buffer the ratio of slopes of the current versus time plots for the decreasing first wave to the increasing second wave is -.65 and at pH 7.98 in a "tris" buffer this ratio of slopes is -.67. The consistancy in the ratio of the slopes with pH allows a correction to be made for the amount of photochemical decomposition which took place before the initial polarographic measurement was made. Table III is a compilation of several polarographic experiments where pH, concentration, and degree of decomposition varied from experiment to experiment. The

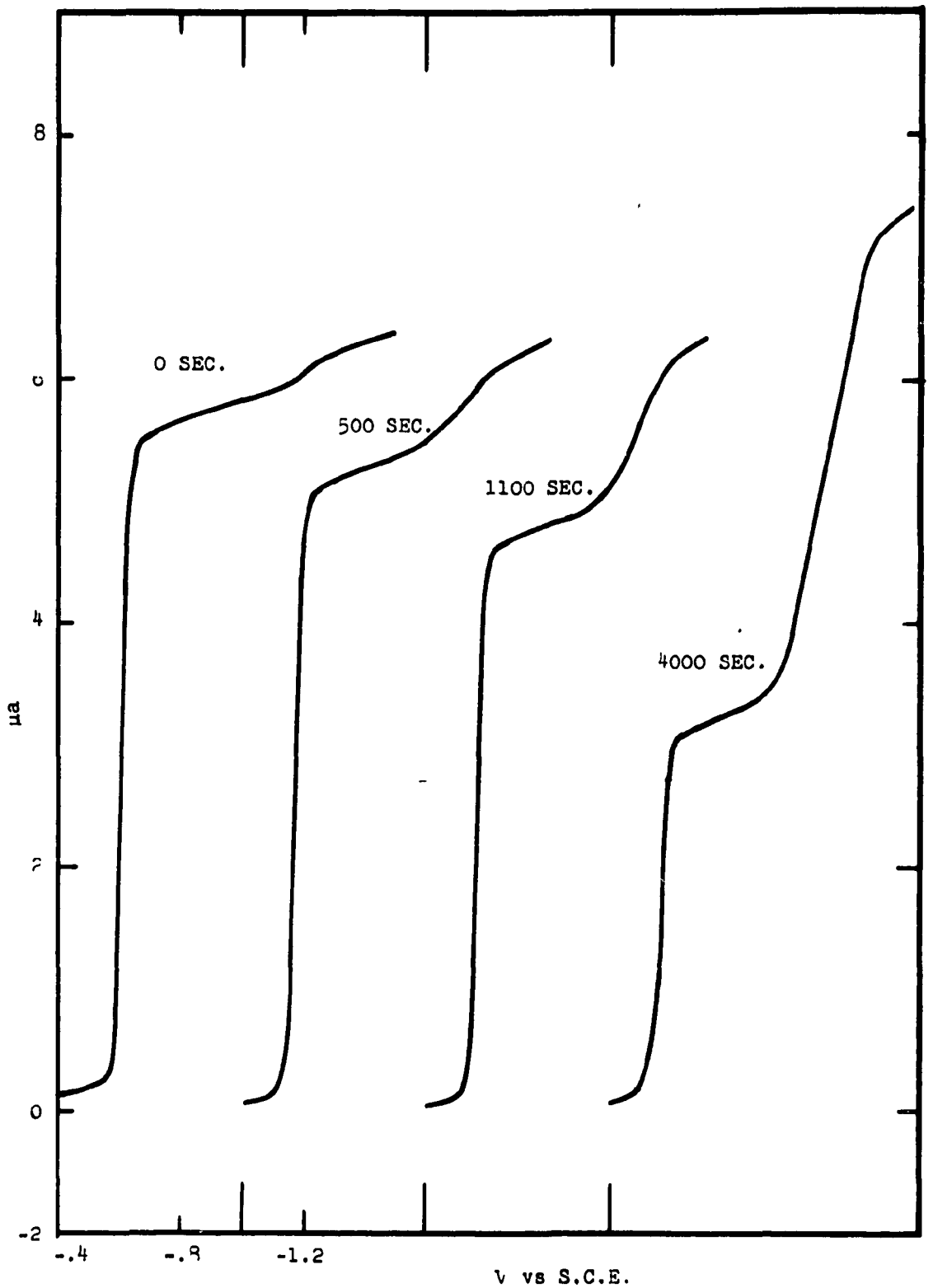


Figure VI

POLAROGRAMS OF $CpFeCpNO_2$ IN 25% EtOH BY VOLUME AT pH 6.47
AFTER SUCCESSIVE EXPOSURES TO LIGHT

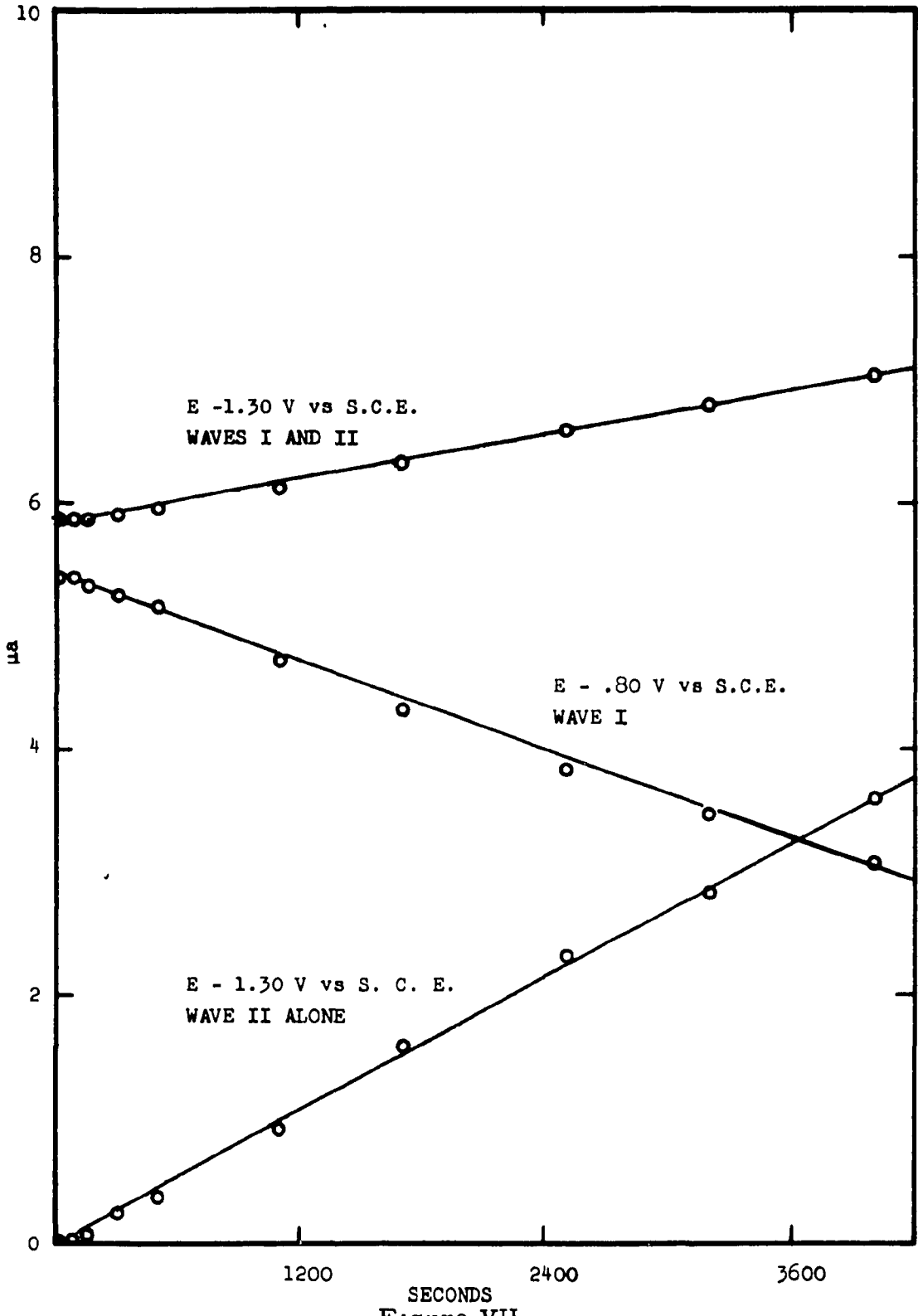


Figure VII

CURRENT FOR A SOLUTION OF $CpFeCpNO_2$ AS A FUNCTION OF LIGHT EXPOSURE AT pH 6.47

pH ranged from 4.0 to 8.6, the concentration varied over a 5-fold range, and the decomposition ranged up to 20% of the initial quantity of nitroferrocene.

A diffusion current constant, I, [67],

$$I = 706\ nD^{\frac{1}{2}} = \frac{i_d}{m^{2/3}\tau^{1/6}C} \qquad (61)$$

was calculated using the appropriate mass flow rate, m, and drop times, τ. The coefficient of variation of these data, $100\sigma/\bar{x}$, is 4.2. Considering that a sample of 15 to 50 milligrams was taken, a pipetting and two dilutions made in the dark, and finally a current measurement recorded, this uncertainty is not excessive. No significant trend in the diffusion current constant with pH or concentration is apparent.

To evaluate the number of electrons in a diffusion-controlled process"n", a value of the diffusion coefficient of the reducible species is required. If an independent measure of the diffusion coefficient is not available, a diffusion coefficient can be assumed, or a comparison of the diffusion current constants for two similar molecules can be made. Because of the structural similarity between ferrocene and nitroferrocene, they should have almost identical diffusion coefficients. The ratio of the diffusion current constants of nitroferrocene to ferrocene should be in the same ratio as the number of electrons in their respective electrochemical processes,

$$\frac{I_1}{I_2} = \frac{n_1}{n_2} \ . \qquad (62)$$

Table III

Diffusion Current Constant and Half-Wave Potentials for Nitroferrocene in Buffered 25% v/v Ethanol-Water Solutions

pH	$E_{\frac{1}{2}}$ vs SCE	M x 10^3	$i_{Observed}$ (a) μa	$i_{Corrected}$ (b) μa	I
4.05	-.455	.195	3.45	3.45	9.32
4.99	-.515	.335	5.51	5.89	9.23
5.28	-.530	.335	5.58	5.83	9.16
6.47	-.597	.323	5.58	5.58	9.07
7.03	Maximum	.809	15.2	15.2	9.93
7.09	-6.25	.195	3.34	3.65	9.86
7.28	Maximum	.518	6.96	8.97	9.13
7.38	-.645	.259	3.92	4.38	8.92
8.12	-.685	.250	3.72	4.10	8.44
8.82	Maximum	.545	8.99	9.40	9.09

$\bar{I}$ = 9.22 100 $\sigma/\bar{I}$ = 4.7%

(a) Observed currents were corrected for residual current.

(b) Corrected currents were corrected for photochemical decomposition (See Text).

Ferrocene has been shown to undergo in several solvents a reversible, diffusion-controlled one-electron oxidation [59, 60, 61]. Using the ratio of diffusion current constants shown in Table IV the nitroferrocene reduction must be a six-electron process. The product expected is aminoferrocene.

Plots of log $\frac{i_d - i}{i}$ versus potential for the rising part of the polarographic wave at different pH's are shown in figure VIII. The slopes of these plots are 37 mv at pH 6.47, 44 mv at pH 7.09, 45 mv at pH 8.16, and 43 mv at pH 8.60. The plot at pH 4.05 is curved, but the initial slope of this plot is 48 mv. The slope of log $\frac{i_d - i}{i}$ plots for a reversible process should be 59/n mv [68]. Applying this relationship to the nitroferrocene wave "n" is found to be 1.3. This is much less than the expected value of 6.0 and implies the process is irreversible.

A plot of pH versus half-wave potential, $E_{1/2}$, for the nitroferrocene wave is shown in figure IX. Several experiments were carried out in which the concentration of nitroferrocene was not determined. The half-wave potentials at the several pH's vs SCE are as follows: pH 7.89, -.678 v; pH 8.18, -.687 v, and pH 8.60, -.717 v. The slope of this plot over the pH range studies was 58 mv/pH unit and $E_{\frac{1}{2}}$ extrapolated to pH of O is -.220 v vs SCE. The variation of half-wave potential with pH for an irreversible process has been interpreted as indicating the number of protons per electron involved in the electron transfer processes up to and including the rate-controlling step:

Table IV

Diffusion Current Constants for Ferrocene and Nitroferrocene in 50% v/v EtOH / H_2O Solutions

	Compound[a]	M x 10^3	I	
1	Ferrocene[b]	.488	1.23	
2	Ferrocene	.343	1.02	
3	Ferrocene	.316	1.19	$\bar{I}$ = 1.16[d]
4	Ferrocene	.418	1.06	
5	Ferrocene	.252	1.29	$100\sigma/\bar{I}$ = 7.5%
6	[c]	.467	1.22	
7	Nitroferrocene	.558	7.16	
8	Nitroferrocene[b]	.459	6.72	$\bar{I}$ = 6.99
9	Nitroferrocene	.418	7.08	$100\sigma/\bar{I}$ = 4.7%

a) Each solution was prepared by independent weighing.

b) Corrected for a 5% photochemical decomposition. All other solutions showed no apparent photochemical decomposition.

c) HNO_3 used as supporting electrolyte rather than $NaNO_3$.

d) A value of 1.27 is reported by Page & Wilkenson [60] in 90% EtOH.

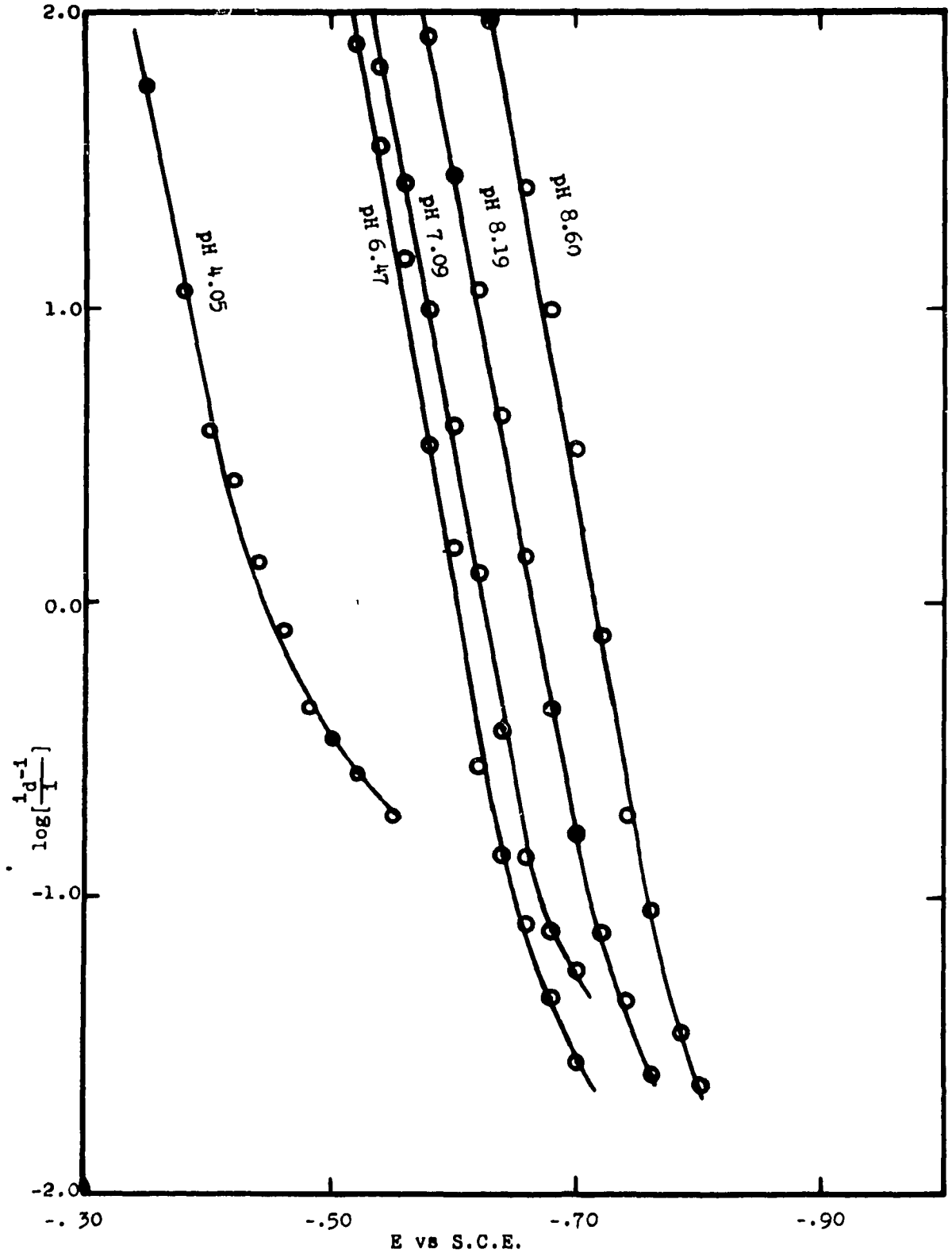


Figure VIII

$\log[\frac{i_d-i}{i}]$ vs E FOR $CpFeCpNO_2$ AT SEVERAL pH's IN AQUEOUS BUFFERS 25% EtOH BY VOLUME

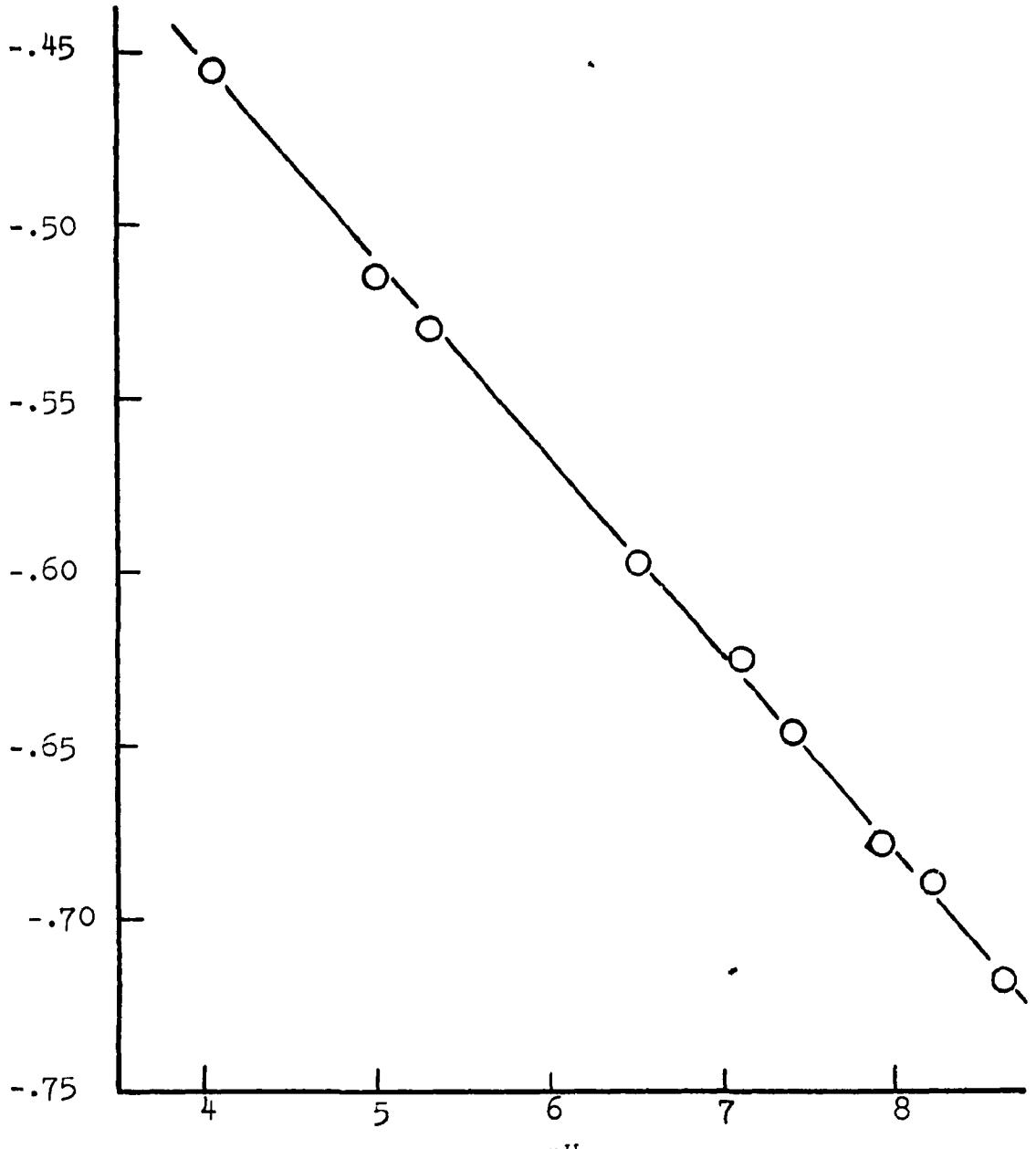


Figure IX

$E_{1/2}$ vs. pH for Nitroferrocene in buffers 25% EtOH by volume

$$\frac{E_{\frac{1}{2}}}{pH} = .0591 \frac{p}{m} . \qquad (63)$$

In the above equation (p) is the number of protons while (m) is the number of electrons involved up to and including the rate controlling step. In the pH range studied, the total number of protons transferred is probably also equal to the number of electrons transferred.

When the photochemical decomposition of nitroferrocene takes place in water, a reasonable set of decomposition products is that shown below:

$$\underset{X}{Cp_2NO_2Fe} + H_2O \xrightarrow{h\gamma} \underset{XI}{CpNO_2^-} + \underset{XII}{CpH} + Fe(II) + OH^- , \qquad (64)$$

where $CpNO_2^-$, XI, is the 1-nitrocyclopentadieneide anion and CpH, XII, is cyclopentadiene. The polarographic characteristics of the sodium salt of 1-nitrocyclopentadieneide, XI, have not been previously reported.

In buffers more basic than pH 7.3, 1-nitrocyclopentadieneide, XI, shows one well defined diffusion-controlled polarographic wave. The half-wave potential of this wave corresponds to the growing cathodic wave observed upon photochemical decomposition. The data for the plot of $E_{\frac{1}{2}}$ vs pH for the growing cathodic wave is shown in Figure X The half wave potentials versus SCE for several solutions of 1-nitrocyclopentadieneide in phosphate and "tris" buffers are the following. pH 7.28, -1.160 v; pH 7.40, -1.170 v; pH 8.00, -1.235 v; pH 8.70, -1.290 v, and pH 8.98, -1.300 v. The half-wave potentials of 1-nitrocyclopentadieneide within the

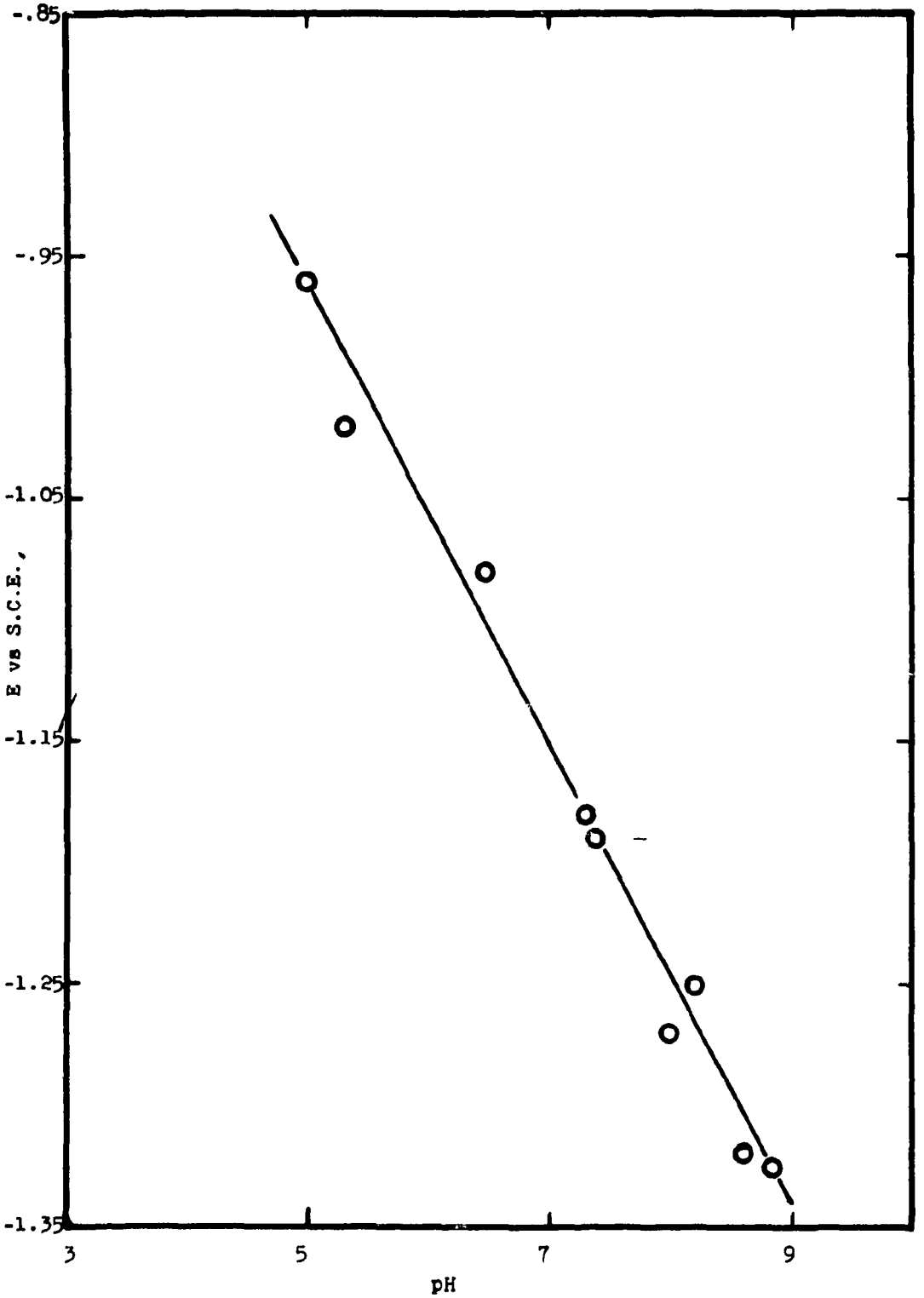


Figure X

$E_{1/2}$ vs pH FOR THE WAVE APPEARING AFTER EXPOSURE TO LIGHT; BUFFERS 25% EtOH BY VOLUME

precision of the potential data correspond to the half-wave potential of the wave that grows on exposure to light. The scatter in the data for the $E_{\frac{1}{2}}$ for the growing wave is greater than that for the original nitroferrocene wave because the percent decomposition was usually never large. Thus the currents for this second wave were usually less than 1 μa; such small currents precluded a more accurate measurement of $E_{\frac{1}{2}}$.

Since 1-nitrocyclopentadieneide, XI, is observed as a product of the photochemical decomposition, the reaction proposed above (64) is believed to be the process which takes place.

The electrochemical reduction of nitroferrocene based on the above evidence is believed to be a six-electron reduction to the corresponding amine, XIII. The reaction is shown below.

$$Cp_2NO_2Fe + 6\,e^- + 6\,H^+ \longrightarrow Cp_2NH_2Fe + 2\,H_2O \qquad (65)$$

The polarography is complicated by a photochemical decomposition of nitroferrocene, (64). Since the radical signal observed in the <u>in situ</u> electrochemical studies of nitroferrocene (vida infra) is never very intense, the second electron in the nitroferrocene reduction must be added more rapidly with respect to the first electron than is the second electron for the several aromatic nitrocompounds discussed above.

The ESR-electrochemical experiments described for the other aromatic nitrocompounds were carried out for nitroferrocene. An ESR signal was observed during the electrolysis of nitroferrocene in both a 1.1 "tris" buffer and in unbuffered solutions. The spectrum was very weak but after half an hour of electrolysis at currents between 100 and 500 μa, the

spectrum became more intense. The signal to noise ratio of the ESR spectrum was never greater than 4:1. The spectrum observed had three lines with a line width of 3 gauss. These lines were separated by 15.1 gauss and had an intensity ratio of 1:1:1. These hyperfine splittings are therefore believed to be due to nitrogen. No additional hyperfine structure was observed. By analogy with the arguments concerning the radical observed during the electrolysis meta-chloronitrobenzene, the radical observed during the electrochemical reduction of nitroferrocene must be the anion radical. From a comparison of nitrogen coupling constants for the nitroferrocene (15 gauss), for the several nitrocompounds discussed above (11-13 gauss), and for the anion radical of aliphatic nitrocomopounds observed by Piette, Ludwig and Adams [14] (23-25 gauss), it is clear that nitroferrocene has a significant aromatic character. For a series of methyl substitute nitrobenzenes Geski and Ragle [69] have observed an increase in the nitrogen coupling constant. The nitrogen coupling constant was observed to increase from 10 to 20 gauss when the nitro group was hindered by increasing the extent of methyl substitution on the 2, 3, 5 and 6 positions. The qualitative argument is that with increasing substitution the O-N-O plane is turned out of the plane of the ring π system, thus increasing localization of the unpaired electron on the nitrogen atom. A nitrogen coupling constant of approximately 23 gauss implies extreme localization of the unpaired electron on the nitro group. A nitrogen coupling constant of 10 to 13 gauss implies that the unpaired electron resides in a delocalized molecular orbital in which the electron spends significant time in the π

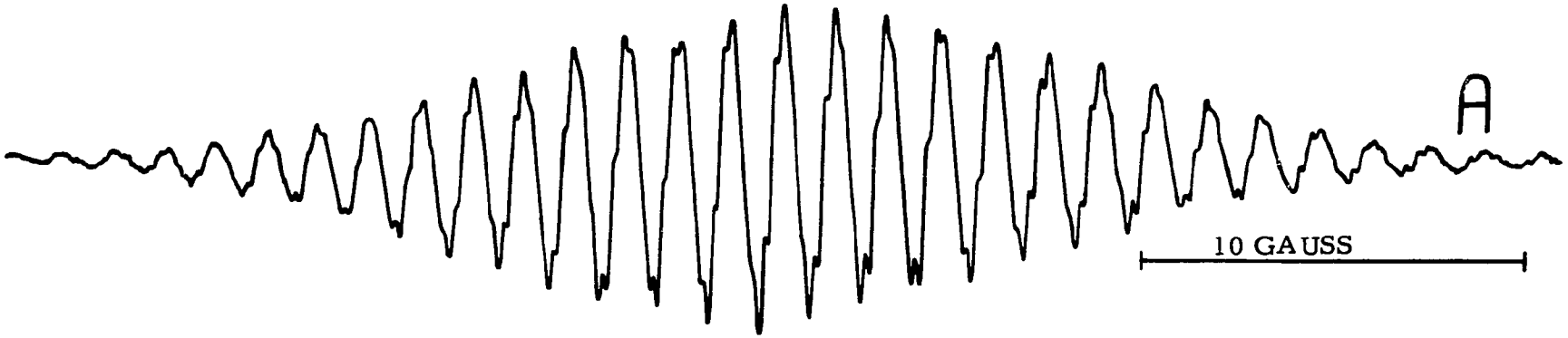
system of the benzene ring. Unpaired electron density for aliphatic nitrocompounds rests primarily on the nitrogen atom [14]. Since the nitrogen coupling constant of nitroferrocene is much closer to the values for aromatic nitrocompounds than to that of aliphatic nitrocompounds, the nitroferrocene anion radical must have a significant aromatic character.

E. N-methylpyridinium Iodide

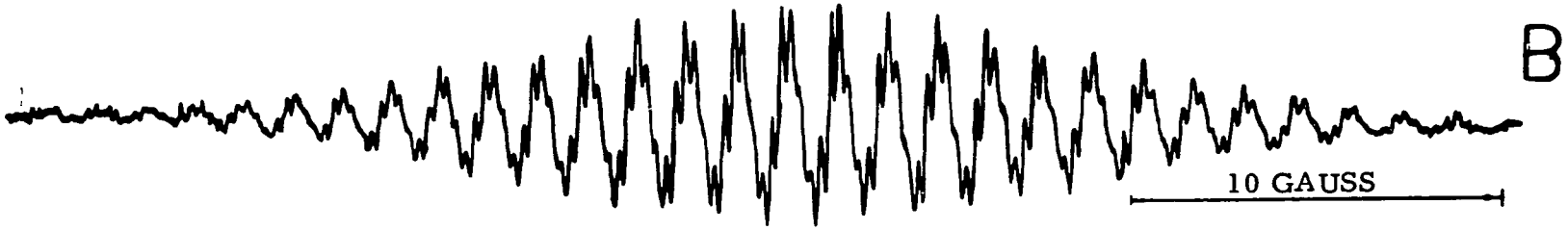
It has been proposed by Tompkins and Schmidt [16] that the polarographic reduction of N-methylpyridinium ion is a one electron per mole process and yields the neutral free radical as a product (7). Emmert [18] had shown on a macroscale that a condensed product was the result of this electrolysis. To test the hypothesis that a free radical does exist and is the intermediate for the condensation, the electrolysis of N-methylpyridinium ion was carried out by techniques already described.

If a basic solution of N-methylpyridinium ion is electrolyzed at -1.5 V vs. S.C.E. for 10 minutes at a current of 400μa (.24 coulombs), a barely detectable ESR signal is present before the electrolysis is discontinued. When the electrolysis is discontinued, this signal grows in less than one hour to an exceedingly intense spectrum. A high resolution ESR spectrum obtained under these electrochemical conditions is shown in Figure XI.

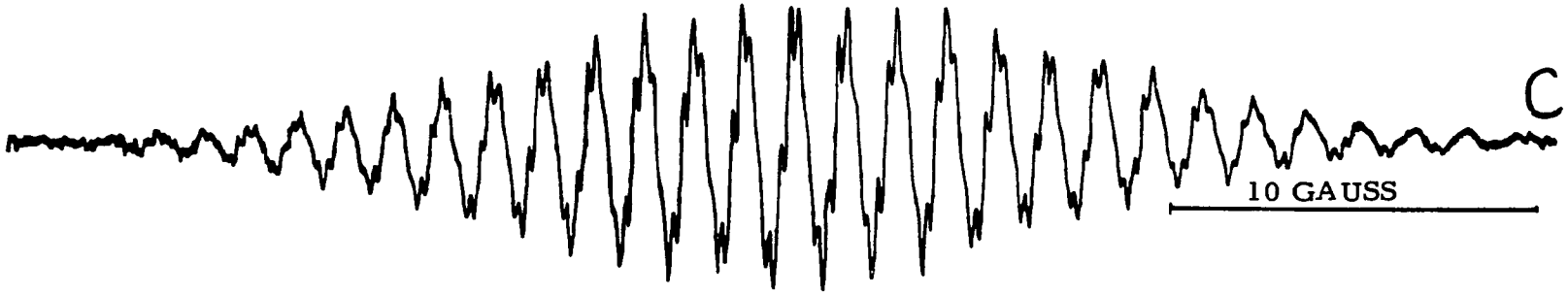
The spectrum which is observed is identical to that obtained from the one-electron chemical reduction of N,N'-dimethyl-4,4'-dipyridyl (methyl viologen) by the method of Michaelis and Hill [70], Figure XI.



ESR Spectrum of methyl viologen radical ion observed after electrolysis of N-methyl-pyridinium ion



ESR Spectrum of methyl viologen radical ion observed after chemical reduction of methyl viologen



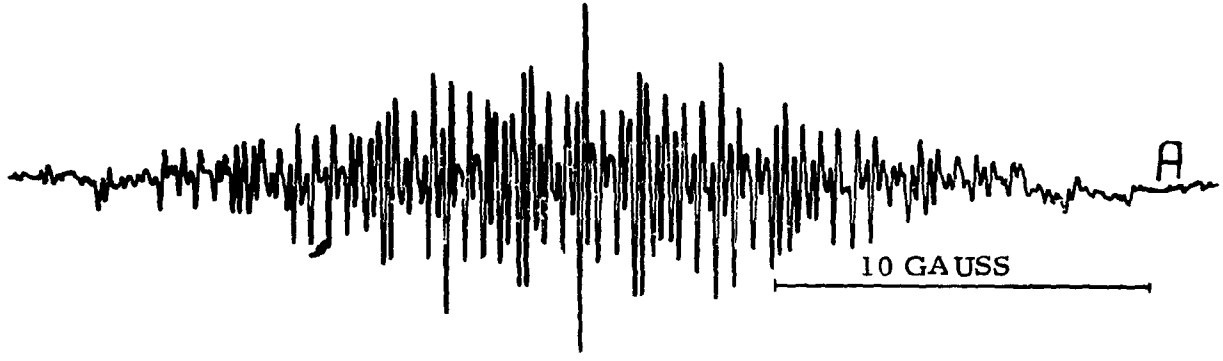
ESR Spectrum of methyl viologen radical ion observed after electrochemical reduction of methyl viologen

Figure XI

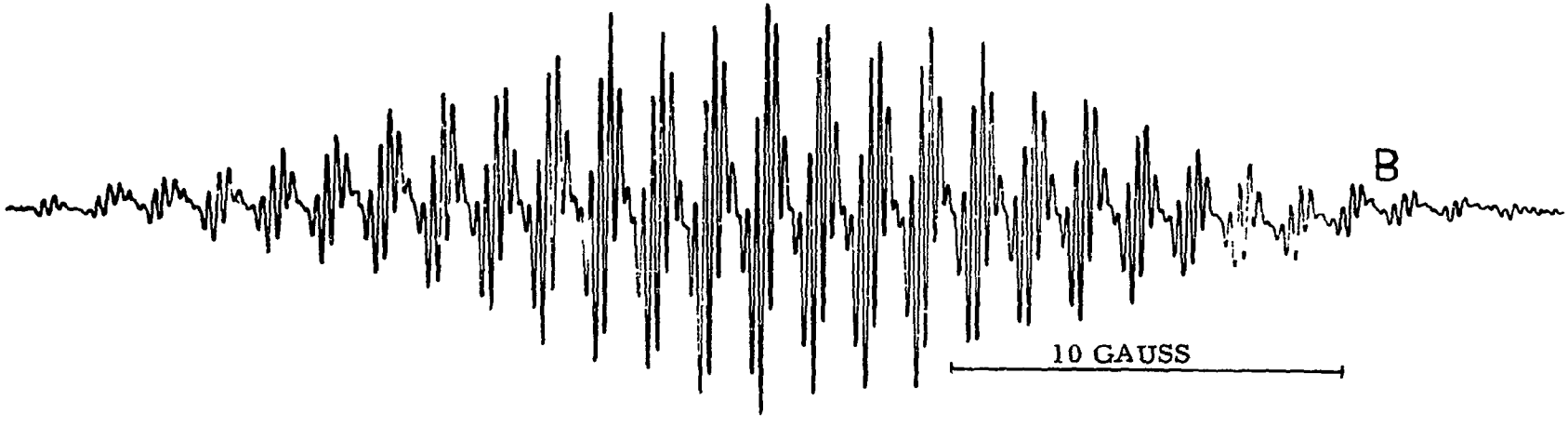
Using the technique of photochemical reduction similar to that described by Brium, Heineken, Brium and Zahlen [71] similar spectra with increased resolution are obtained, Figure XII. The same spectrum is also observed from direnT electrochemical reduction of methylviologen at -.70 V vs SCE [72], Figure XI. When prepared in carefully degassed solutions, the radical observed by all four preparative methods was stable for a period of at least one day.

Based upon all the available polarographic evidence there appears no doubt that on the polarographic time scale, 5 seconds, the reduction of N-methylpyridinium ion requires one electron per mole [16, 17, 73]. This was verified by an independent determination of the diffusion coefficient, "D", of N-methylpyridinium ion [74]. The number of electrons was calculated to be one after substitution of "D" into the diffusion current constant [67] for N-methylpyridinium ion, ($I = 1.95 \pm .05$ [16]).

Based on the observed spectrum and its growth when electrolysis is discontinued the product of electrolysis must have dimerized and then, via a series of homogeneous chemical steps, yield the observed radical. Since no large ESR signal due to a one-electron reduced product of the parent compound is observed during the electrolysis, the dimerization must take place rapidly if the electrochemical step is a one-electron process. For a one-electron process the current passed is equivalent to 2.7×10^{15} radicals per second for a period of 10 minutes or 1.6×10^{18} radicals. The extremely small ESR signal observed during the electrolysis could at most correspond to 1×10^{14} radicals These data indicate that if the reduction is a one-electron process that dimerization must be fast.



ESR Spectrum of 4,4' dipyridylium radical ion from photochemical generation.



ESR Spectrum of methyl viologen radical ion from photochemical generation.

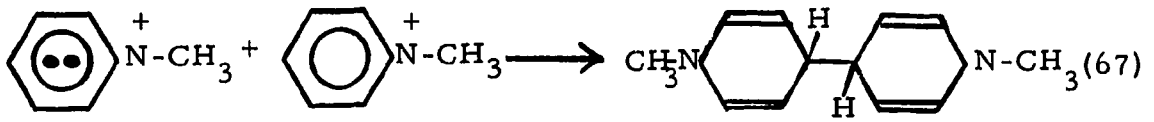
Figure XII

This observed ESR signal must be the sum of two signals: one is due to some N,N'-dimethyl-4,4'-dipyridyl radical ion (methyl viologen radical ion) formed chemically during the electrolysis, while the second is due to the one-electron reduced product of N-methylpyridinium ion. Because of the low signal intensity high resolution ESR spectra could not be recorded during the electrolysis to determine if the observed signal was indeed the sum of two signals. A large signal due to methyl viologen radical ion is not possible during the electrolysis because at -1.5 V vs SCE this radical ion is reduced still further at the electrode surface [72].

It is quite possible that the electrochemical reduction of N-methylpyridinium is not a single electron transfer process and a rapid dimerization, (7) and (8), as has been proposed previously [16, 19, 73]. The process could be a two electron transfer process followed by a rapid chemical reaction of the two electron reduced species with the unreduced species If this were the case, the ESR spectrum observed prior to discontinuing electrolysis is due solely to methyl viologen radical ions. This second possible scheme is shown below:

(66)

II



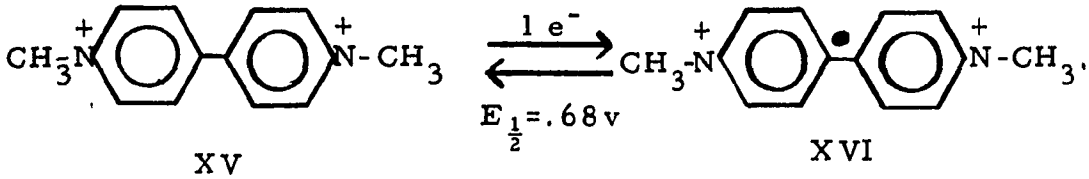
(67)

II XIV

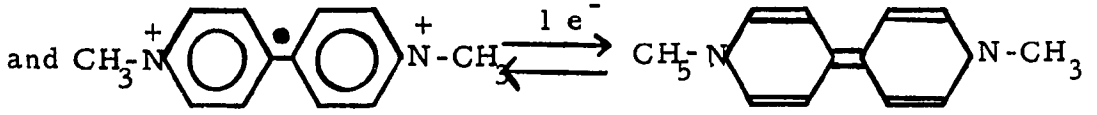
In order to differentiate between the two electron reduction scheme above, (66) and (67), and the one electron scheme given earlier, (7) and (8), a detailed analysis of the current-potential-time curves in the potential region before complete concentration polarization is achieved must be carried out. Schwarz [75] has carried out some calculations considering only the one electron model and a not too rigorous model for diffusion. He concluded that the data were not inconsistant with his model, but the agreement between his theoretical curves and those experimentally observed was not very good. He did not perform calculation for the two electron model, (66) and (67).

Regardless which mechanism is operating (7) and (8), or (66) and (67) a dimer must be formed [18] and such a formation must be sufficiently fast to allow bulk chemical formation of the observed methyl viologen radical.

Current-voltage curves on the gauze electrode after the electrolysis was discontinued show the presence of only three electroactive species. They are the original N-methylpyridinium ion and both methyl viologen, XV, and methyl viologen radical-ion, XVI, (Figure XIII). Polarograms of the catholyte of macro-scale electrolysis of N-methylpyridinium ion (constant current) showed a similar set of electroactive species. The half-wave potentials of the observed waves (-.69 v and -1.02 v vs. SCE) agree quite well with -.68 v and -1.04 v vs. SCE reported in the literature [72]. The proposed reactions are (68) and (69) shown below·

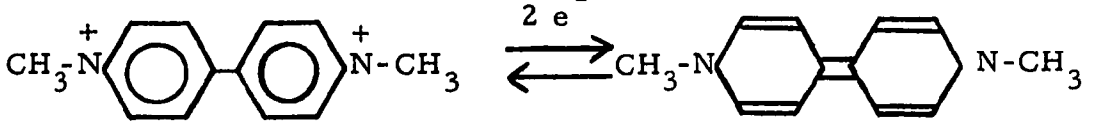


XV XVI (68)



XVI XVII (69)

Further confirmation of the chemical nature of the observed electroactive species was obtained by polarizing the gauze electrode at -.58 v, -.85 v and -1.08 v vs. SCE. At the most anodic potential the ESR signal decreased very rapidly with time (17% decrease in 7 minutes at 3μa anodic current), therefore the process is an oxidation of the radical-ion to methyl viologen. At -.85 v vs SCE the ESR signal grew with time (4% increase in 5 minutes at 5μa cathodic current). This process is therefore a reduction to the radical and is a reduction of the methyl viologen itself. It has been proposed [72] that the second reduction process of methyl viologen is the two electron process shown below.



XV XVII (70)

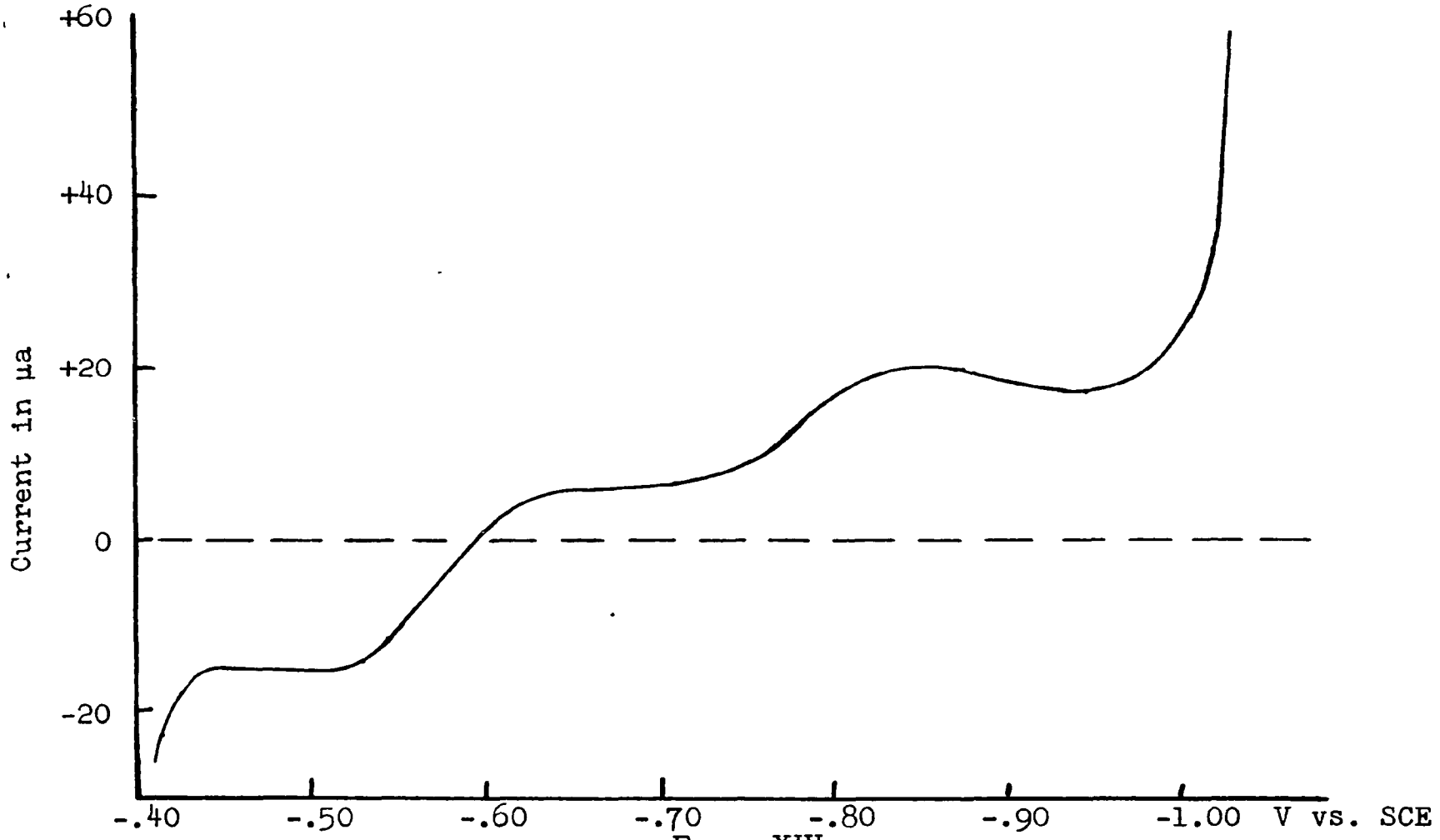


Figure XIII

Current voltage curve on the gauze electrode after a partial electrolysis of N-methylpyridinium ion. The electrode was mounted in the Varian aqueous sample cell in the cavity of the Varian ESR Spectrometer

The same product, XVII, is expected if the methyl viologen radical-ion XVI is reduced by a one electron process.

The relatively large quantities of methyl viologen observed in the catholyte during electrolysis in the ESR cell, Figure XIII, and on a macro scale could not have come from oxidation of methyl viologen radical ion by traces of dissolved oxygen. The solutionsfor these experiments were scrubbed free of dissolved oxygen with Linde HP nitrogen. The nitrogen had been previously passed through a vanadous sulfate solution to remove the traces of oxygen present in the nitrogen. This oxygen scrubbing solution was contained in a gas wash bottle and was constantly being regenerated by zinc amalgum which was also in the bottle. Scrubbing of the nitrogen should leave the oxygen content in the catholyte below 10^{-7} M. The quantity of dissolved oxygen present in the solution volume of the aqueous sample cell ($\sim$. lcc) used in the ESR experiment is not sufficient to allow oxidation of an appreciable quantity of methyl viologen radical ion to methyl viologen. The current voltage curves for both the macro scale and ESR electrolysis experiments after terminating the electrolysis always show a concentration of methyl viologen comparable to that of the radical ion. This presence of both species in a volume element already oxygen free is a clear indication that both methyl viologen and its radical ion are produced homogeneously.

Further evidence for the homogeneous growth of the methyl viologen and its corresponding radical-ion is provided by the following observations. First, the polarographic waves of both methyl viologen and its radical ion occur at more anodic potentials than the reduction of N-methylpyridinium

ion. Thus if these species were produced at the electrode surface during the reduction of N-methylpyridinium ion they could never escape, but rather they would be reduced immediately. Second, the intensity of the ESR spectrum of the radical-ion is observed to grow when the electrolysis is discontinued. This growth of the radical ion after the electrolysis is discontinued is also observed during a macro-electrolysis. In a macro-electrolysis the blue color of the radical-ion is observed to deepen after the electrolysis is discontinued.

In order to rationalize the presence in the catholyte of both methyl viologen and its corresponding radical ion, at least two homogeneous chemical reactions must be taking place. The first reaction to take place must be a redox reaction involving the condensed product of the initial one electron reduction, N,N'-dimethyl-4,4'-dihydro-4,4'-dipyridyl XIV. This species must be converted to either methyl viologen XV or to the methyl viologen radical-ion, XVI. In order to convert XIV to methyl viologen, XV, two protons and four electrons must be lost, while to reach the radical-ion, XVI, two protons and three electrons must be lost.

The second chemical reaction must involve an electron transfer reaction between two of the three oxidation states of methyl viologen which are present in the catholyte during electrolysis in the ESR cavity. To test this hypothesis an electrolysis of a solution several millimolar in methyl viologen, .1M in Cl^- and .040 M in OH^- was carried out. The electrolysis vessel was the "H-cell" described previously. The cathode was a mercury pool, $\sim$1 cm^2, at the base of the cell. The reference was the SCE built into

the cell while the anode was a Ag/AgCl wire wrapped about the capillary of the dropping mercury electrode. The dropping electrode was used as a probe to take current-voltage curves of the catholyte during electrolysis. The potentiostat employed has been described by Enke [76].

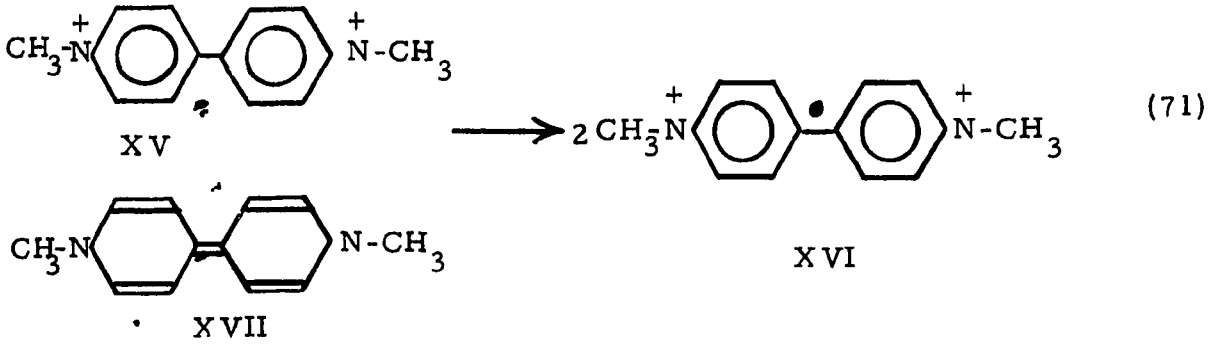
The potential of the pool was made -1.40 v vs. SCE. and currents of .1 to .2 ma were drawn. It was observed that the solution several millimeters above the electrode became blue, but the solution closer to the electrode solution interface remained clear. When the electrolysis was terminated, all the solution in the vicinity of the electrode became a dark blue. The blue color eventually diffused throughout the entire cell.

The solution prior to electrolysis was purged at O_2 by using N_2 previously passed through a vanadus sulfate solution to remove the traces of O_2 in the N_2. During and after the electrolysis N_2 was continuously passed over the surface of the catholyte.

At -1.40 v vs. SCE. methyl viologen XV is reduced with two electrons to the doubly reduced species XVII as shown by equation (70). A potential of -1.40 v is well on the diffusion plateau of a polarographic wave, and therefore the surface concentrations of both methylviologen, XV, and radical ion, XVI, are zero. Further that radical ion, XVI, cannot be the product of the electrolysis.

Current voltage curves of the catholyte at the dropping electrode showed a mixed anodic and cathodic process with an $E_{\frac{1}{2}}$ of -.70 v vs SCE and a second more cathodic wave. The mixed anodic and cathodic process corresponds to the reversible oxidation-reduction reaction (68). The second

cathodic process corresponds to reaction (69). The observed blue color clearly demonstrates the presence of the radical ion, XVI. This species could only come about by a homogeneous chemical reaction between unreduced methyl viologen XV and its doubly reduced state XVII. The proposed reaction is shown below:



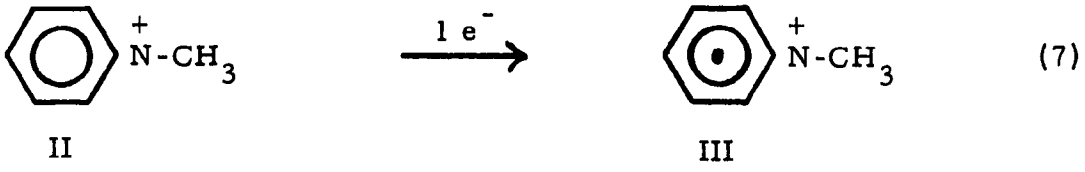
XV + XVII → 2 XVI (71)

The origin of methyl viologen XV must be a homogeneous chemical reaction involving the condensed product, XIV, of the initial electrochemical reduction of N-methylpyridinium ion. Since the methyl viologen radical ion is observed to grow after the electrolysis is discontinued and is present in only small amounts during the electrolysis, it is felt that the homogeneous reaction yields only the unreduced methyl viologen as its product. The chemical reaction (71) which produces the radical ion, XVI, is believed to be an electron transfer reaction between the doubly reduced, XVII, and unreduced methyl viologen, XV.

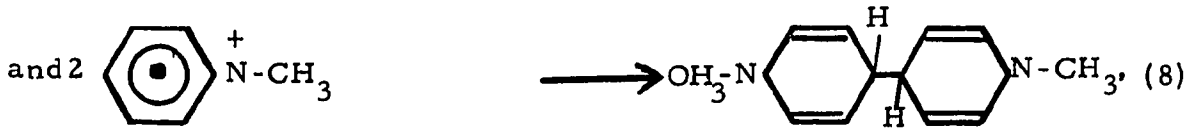
The doubly reduced methyl viologen, XVII, is produced from both the methyl viologen and its radical-ion at the electrode during the electrolysis. The very cathodic potential of the gauze electrode (-1.5 v vs. SCE) is sufficient to carry out such a reduction. At present it is not possible to clarify in more detail the nature of the chemical reactions which yield the methyl viologen,

but a mechanism consistent with all the experimental observations is that shown below. This mechanism must be divided into two parts. The first part is a series of heterogeneous electron transfer steps and rapid chemical reactions which take place on or in the immediate vicinity of the electrode surface. These reactions cease to take place when the electrolysis is discontinued. The second part of the mechanism involves a series of homogeneous chemical steps which take place at distances removed from the surface of the electrode. These reactions occur during and after electrolysis.

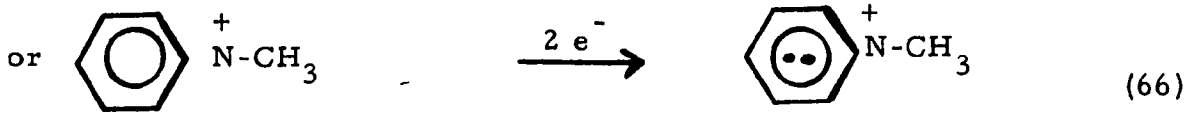
During electrolysis the reactions which take place at or in the immediate vicinity of the electrode surface are:



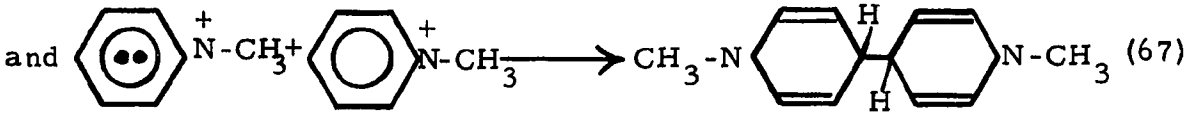
II III (7)



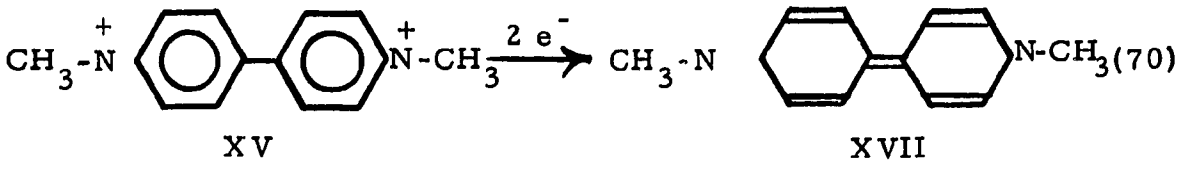
III XIV (8)



II (66)

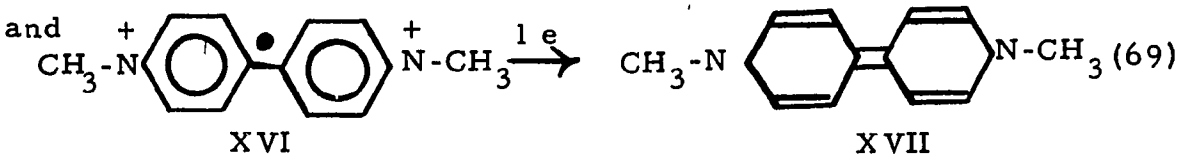


II XIV (67)



XV XVII

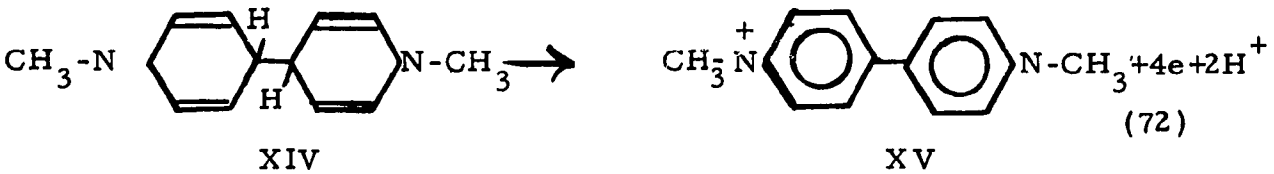
(70)



XVI XVII

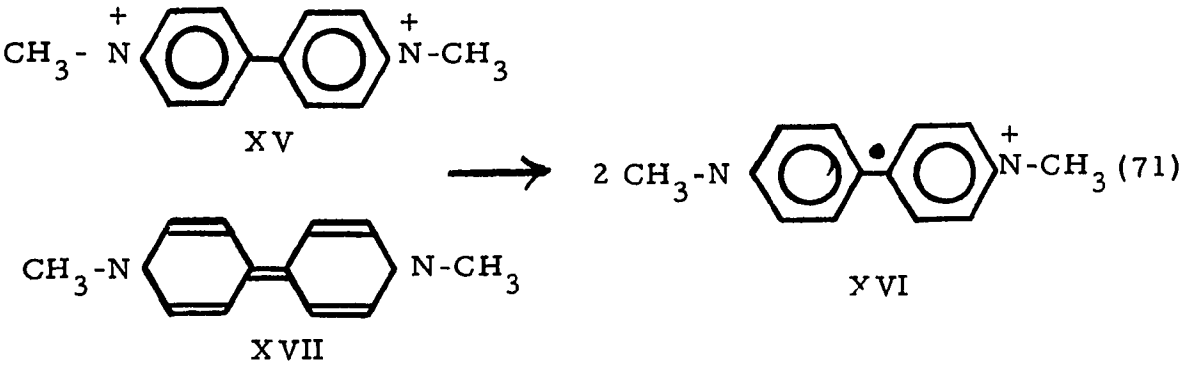
(69)

The chemical reactions which are believed to take place at distances remote from the electrode surface are:



XIV XV

(72)



XV XVI XVII

(71)

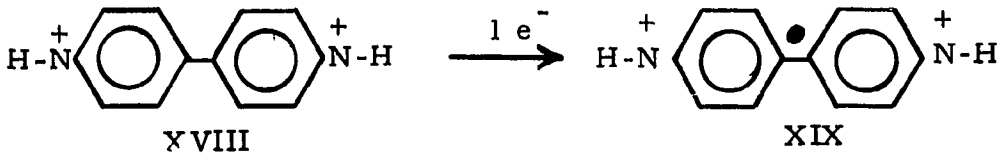
Considering some observations by Schwarz [75] which demonstrated in a quantitative fashion that two ethyl viologen radicals dimerize ($K_f = 2.65 \times 10^{-3}$), it is quite possible that dimers of methyl viologen also exist.

The several oxidation states of the viologen system bear more than a passing resemblance to the quinone, hydroquinone, semiquinone, and

quinhydrone system. Such a suggestion has already been made by Michaelis [77, 78].

F. 4,4'-dipyridylium Ion

It has been proposed [79] that the first wave in the polarographic reduction of 4,4'-dipyridylium ion, XVIII, is a one-electron reduction yielding the corresponding radical ion XIX,



XVIII XIX (73)

In order to test this proposed scheme an electrolysis of XVIII was carried out by methods already described.

1. ESR spectra

A radical was indeed observed during electrolysis in both acetate buffers and strong acid. Its spectra is shown in Figure XIV. No spectrum was observed in buffers of pH 7.5. The observed spectrum is consistent with the following set of coupling constants: 2 equivalent spins of 1, a_N=3.57 gauss, 2 equivalent spins of 1/2, a_{H_1} = 4.06 gauss, and 8 equivalent spins of 1/2, a_{H_2} = 1.53 gauss [80]. Spectra identical to those from electrochemical generation were obtained by chemical generation using the method of Michaelis and Hill [70].

The spectrum in the lower part of Figure XIV was synthesized by assuming the hyperfine splitting constants given above and Lorentzian line

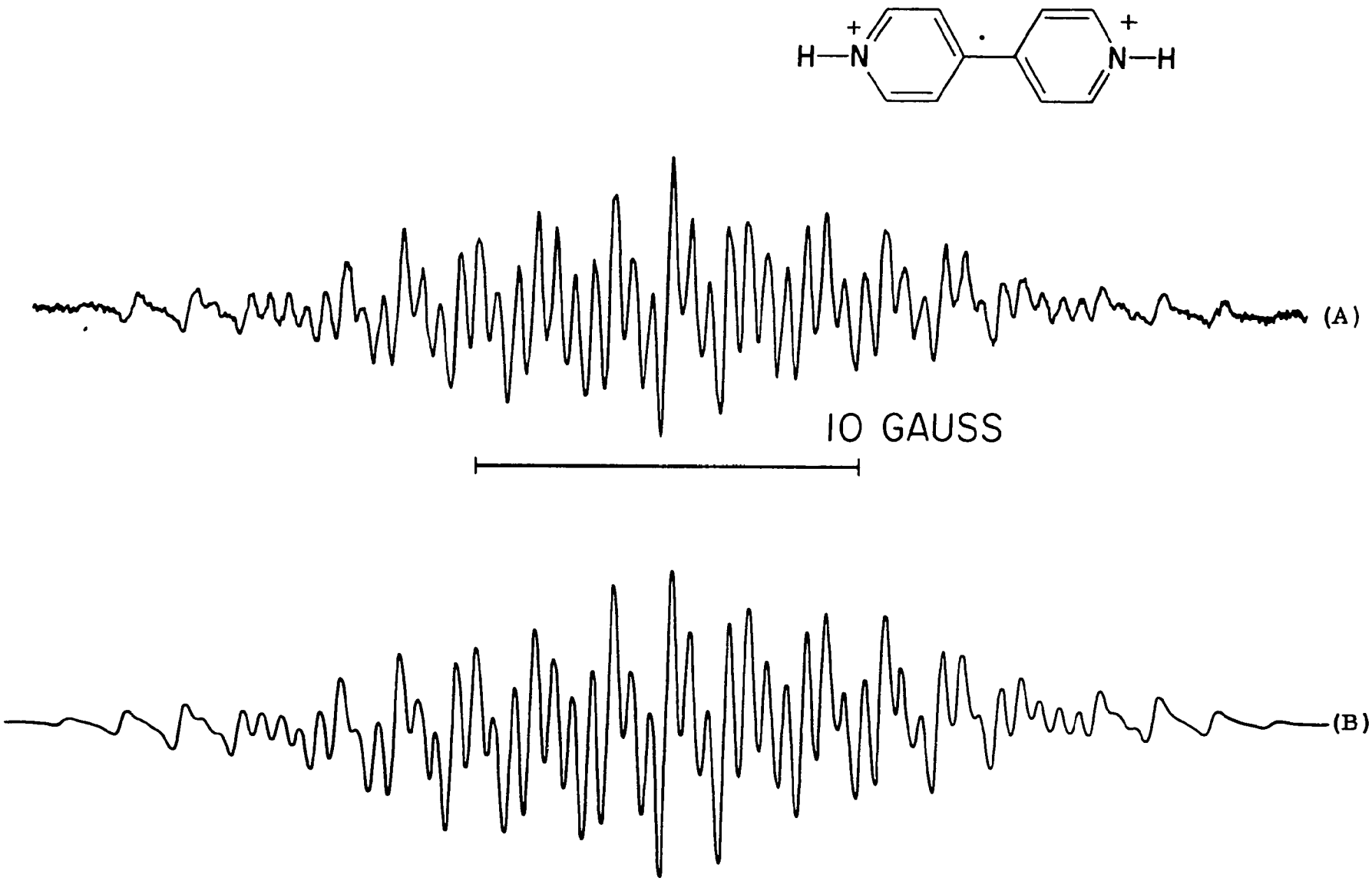


Figure XIV. Observed (A) and calculated (B) ESR spectrum of 4, 4' dipyridylium radical ion (see text).

shape with a width of 0.36 gauss at the point of maximum slope. Calculation of points along the curve was carried out by the Illiac computer using a program kindly supplied by Dr. R. M. Deal. The computer output was in the proper form to be used as input for the Pace Model 3033B-1 Dataplotter. It should be noted that the calculated spectrum reproduced the experimentally observed spectrum in both line position and relative line intensity. The calculated spectrum also has no lines which were not experimentally observed. For the reason discussed below the largest proton coupling constant, a_{H_1}, is assigned to the protons bonded to the nitrogens. If D_2O rather than H_2O is used as the solvent, the spectrum obtained differs from the spectrum in H_2O by the omission of the largest hyperfine splitting; therefore this hydrogen atom must be capable of exchange with the environment. Of the several types of hydrogen present in this compound the only type that could reasonably exchange with its environment is the hydrogen bonded to the nitrogen. In D_2O there is an indication that the eight ortho- and meta- protons are in reality not equivalent, and that the mean value of their splitting constants is closer to 1.45 gauss than to the 1.53 gauss given above.

Recently Briun, Heineken, Briun and Zahlan [71] have reported an ESR spectrum of the 4,4'-dipyridylium radical ion. The spectrum of the radical obtained from photochemical generation in 95% EtOH is similar to that in Figure XIV except for higher resolution. These authors report that a consistent set of splitting constants are a_N = 3.56 gauss for two equivalent nitrogens, a_{H_1} = 7.14 gauss for a set of two equivalent protons, a_{H_2} = 1.43 gauss for a set of four equivalent protons, and a_{H_3} = 0.48 gauss for another

set of four equivalent protons. The experiment of Briun, Heineken, Briun and Zahlan was repeated in this laboratory. The spectrum recorded after a five minute exposure to sunlight was identical to theirs except a further increase in resolution was attained, Figure XII. This spectrum is consistent with those electrochemically and chemically generation radicals observed in this study except that the smallest proton coupling constant a_{H_2} = 1.53 gauss is no longer sufficient to describe the spectrum. The eight protons with splitting constant a_{H_2} are now believed to be two sets of four protons each. The coupling constants for these two sets of four protons are a'_{H_2} = 1.63 and a_{H_3} = 1.45. The line width of the center line using photochemical generation is observed to be 0.090 gauss. It is to be noted that the average of a'_{H_2} and a_{H_3} is 1.53 gauss and the difference between a'_{H_2} and a_{H_3} is well within the line width of 0.3 gauss obtained by the earlier methods. The increase in line width in the electrochemical experiments is believed to be due to dissolved O_2 [33] or magnetic field inhomogeneity. Magnetic field inhomogeneity is less of a problem with the photochemical experiments than electrochemical experiments since the sample was in a 3 mm o.d. capillary rather than in the aqueous sample cell. Dissolved O_2 in the photochemical experiments was removed by cyclic freeze drying and evacuation.

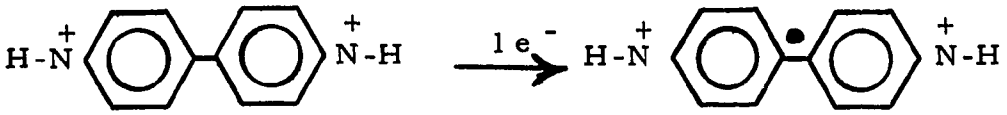
Since the ESR spectrum observed has a line in the center of the spectrum, the sum of the maximum value of the nuclear spins for each set of atoms in the radical which causes this absorption spectrum must be even, thus there must be an even number of protons in the radical. Since

both nitrogens in the unreduced 4,4'-dipyridylium ion are protonated at the pH used in these experiments, since a spectrum identical with that experimentally observed has been calculated based on only ten protons (eight ortho and meta protons and two protons on the nitrogens), and since three independent preparative techniques yield the same radical, the radical which is observed is consistent with being the one-electron reduced radical of the doubly protonated 4,4'-dipyridylium ion, XIX.

2. Electrochemistry and the electrochemical mechanism

Figure XV shows on the same potential scale the polarographic wave of XVIII and the relative efficiency for the formation of the free radical, XIX, for a micro-scale controlled potential electrolysis in the ESR cell. If the free radical is the final product of the electrolysis, the efficiency for its formation would be constant throughout the potential region corresponding to the first polarographic wave, which is not the case. Actually the concentration of free radical falls to zero at the top of the polarographic wave.

A conclusion consistent with the above experimental evidence is that the observed radical is an intermediate in an overall two-electron reduction to the corresponding di-hydrocompound, XX, as shown below:



XVIII XIX (73)

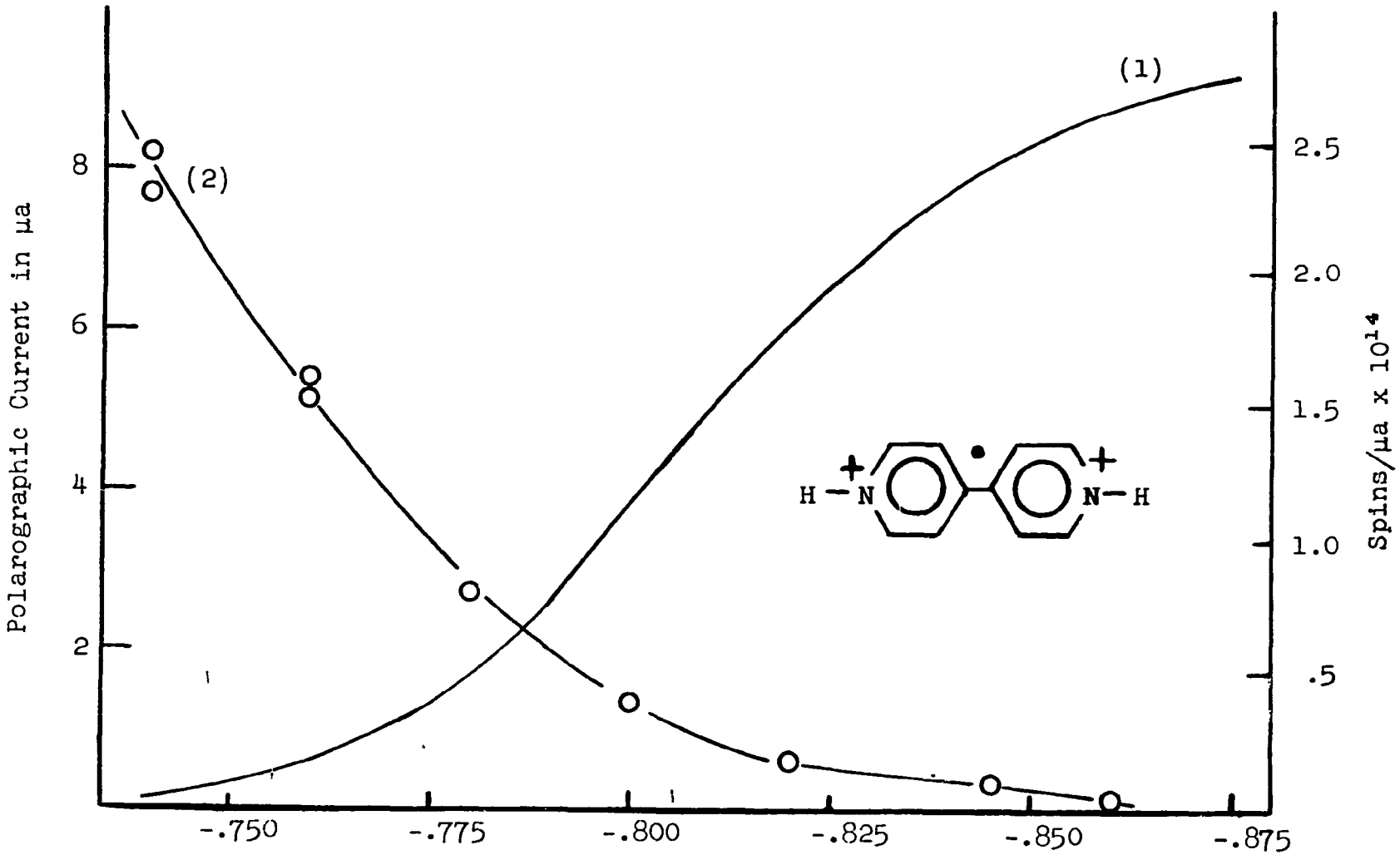
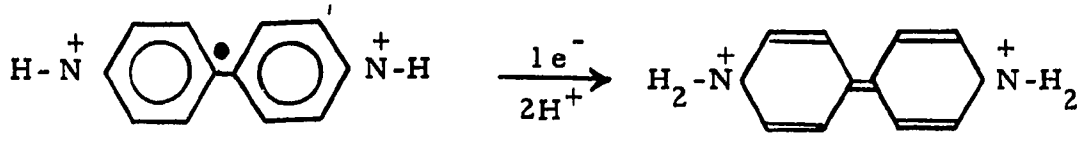


Figure XV

Polarogram of 4,4'-Dipyridylium ion (1) in μa on the same potential axis as relative efficiency for radical formation (2) in units of steady state spins per μa of electrolysis current in pH 4.4 acetate buffer.

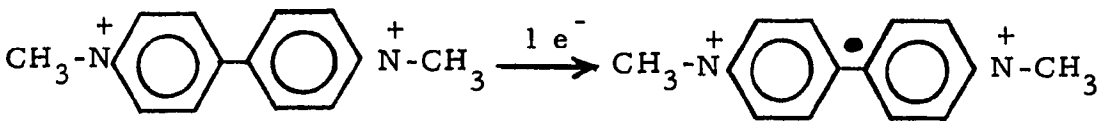


XIX XX (74)

The above scheme requires that efficiency for the radical formation become less toward the top of the wave and fall to zero at potentials which correspond to the diffusion plateau of the polarographic wave. This scheme is consistent with the observed ESR intensity-potential data, Figure XV.

The electrochemical reduction of 4,4'-dipyridylium ion is therefore believed to be an overall two-electron process in which the first electron is added at a rate comparable to that of the second. The radical which is observed is thus an electrochemical intermediate which has escaped from the electrode surface. This scheme is an example of consecutive one-electron reductions discussed earlier, (37) to (40).

A similar conclusion is reached if the polarographic behavior of 4,4'-dypridylium ion, XVIII, and N,N'-dimethyl-4,4'-dipyridyl, XV, are compared. The first polarographic wave of XV has been shown to be a reversible one-electron process [72, 75]. The product of the reduction is the corresponding radical ion, XVI, as shown below:



XV XVI (70)

The half-wave potential for the reduction of XV is pH independent as would be predicted since no protons are involved in the reduction. If the reduction

of XVIII was also a one-electron process, the half-wave potential of this reduction should also be pH independent. The data of Falqui and Secci [81] clearly show that this is not the case. In the pH region below 4.0, where both nitrogens are protonated, ($K_1 = 6.8 \times 10^{-4}$ and $K_2 = 1.5 \times 10^{-5}$ [82]), the half-wave potential is definitely pH dependent (46 mv/pH unit). This intermediate dependence between 1 and 2 protons per electron is that predicted by reactions (73) and (74).

The first step in the overall reduction of 4,4'-dipyridylium ion (60) should be insensitive to pH changes in a pH region where the principle unreduced species is doubly protonated (pH = 3.5). The second step in the mechanism should be pH dependent. A pH dependence of the polarographic wave is observed [77, 81]. A marked change in the polarographic behavior is also observed at pH > 5. In this pH region a large fraction of the 4,4'-dipyridyl exists as the free base or the singly protonated species [82]. At a pH of 7.5 no ESR signal was observed under the usual conditions. This failure to observe a radical suggests that in the case of unprotonated 4,4'-dipyridyl the second electron is added very rapidly with respect to the first electron or that the unprotonated radical is very unstable.

Electrochemical mechanisms which involve quinone, semiquinone, hydroquinone and quinhydrone-like species and their several inter-related equilibra [77, 78] are not consistent with the ESR intensity-potential data.

The ESR signal of 4',4'-dipyridylium radical ion is observed to decay when the electrolysis is discontinued; therefore, some description of radical decay is necessary. Decay curves of the ESR signal at potentials which correspond to the foot of the polarographic wave are shown in Figure XVI.

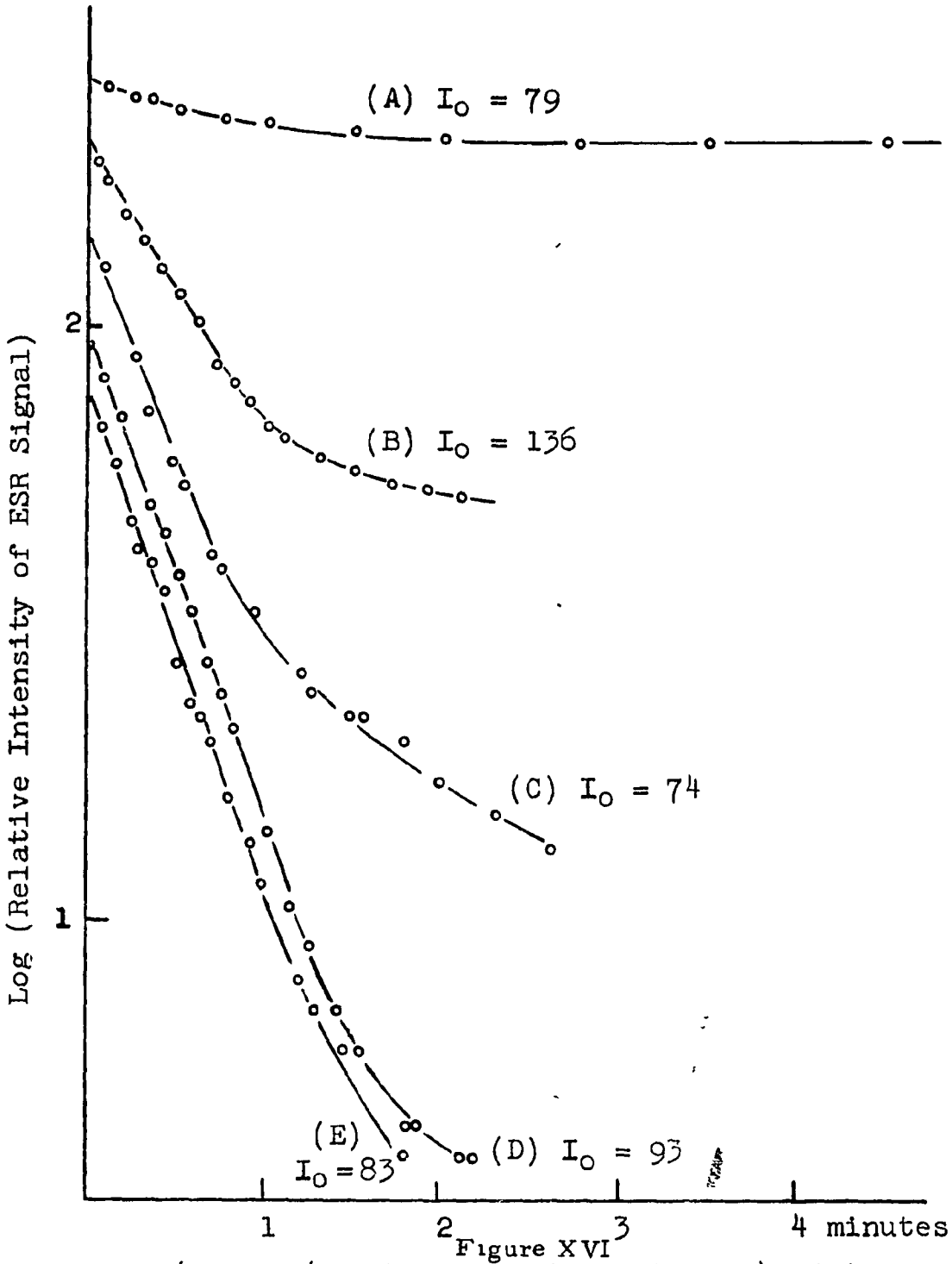


Figure XVI

Log (Relative Intensity of ESR Signal) After termination of electrolysis for 4,4'-dipyridylium radical ion versus time. Curve A is the decay after the longest electrolysis while curve E is the decay shortest electrolysis. I_o is the zero time intercept of the signal intensity.

At these potentials when the duration of the electrolysis is short, the decay of the signal is first order during the early stages of decay, but departs from this behavior after about three half-lives. In those experiments where a long electrolysis was employed prior to the decay study, departure from first order decay occurrs sooner than when a short electrolysis was employed. The decay data for runs A and B were taken after an electrolysis at 10μa for less than five minutes; the signal decay is first order for four half-lives with $\tau_{\frac{1}{2}}$ of 44 seconds. For run C, which was electrolyzed for one hour at 15μa, significant departure is observed after two half-lives (90 seconds). In run, D, which was electrolyzed at 25 μa for about one hour, significant departure from first order decay is observed to take place during the second half-life. In run, E, for which the electrolysis lasted three hours at 40μa, very little decay was observed to take place when the electrolysis was discontinued. Studies on different gauze electrodes appear not to alter these observations.

In the experiments where high resolution ESR spectra were recorded, regardless of the extent of electrolysis, there never was an indication that a second radical was produced.

Decay studies for radicals resulting from an electrolysis carried out at more negative potentials than those above are more complex. The ESR signal is observed to grow for a short time after the electrolysis is discontinued, however, after one or two minutes the signal begins to decay. The decay of the ESR signal is slower than the decay at the less cathodic potentials At these more negative potentials the intensity of the steady state

ESR signal during electrolysis is smaller while the steady state current is larger.

The magnitude of the signal increase, the decay rate after the maximum signal attained, and the rate of attainment of this maximum signal all vary with electrode potential. The largest percent increases in signal intensity after terminating the electrolysis is observed at the most negative potentials. The time after terminating the electrolysis necessary to reach the largest ESR signal appears to increase while the rate of decay of the ESR signal decreases with increasing cathodic polarization.

Current-voltage curves with a dropping mercury electrode have an adsorption prewave. The current of the prewave for a 10 millimolar solution of 4,4'-dipyridylium ion is .14 μa. Such small currents imply the formation of a monolayer of adsorbed material rather than a multilayer formation. Electrocapillary curves for solutions of 4,4'-dipyridylium ion show marked decreases in the drop time at potentials more negative than the half wave potential. This decrease in drop time and also a series of experiments employing rapid recording of the individual current-time behavior of growing drops indicate that a second adsorption process takes place almost at the very top of the polarographic wave. The adsorption prewave is probably due to the free radical, but the second adsorption process at the top of the wave could not be due to the free radical since no radical is observed at these potentials in the ESR experiments. This second process must be an adsorption of the two electron reduced product.

Current-time curves on the stationary gauze electrode are well behaved for all other systems studied and for 4,4'-dipyridylium ion solution

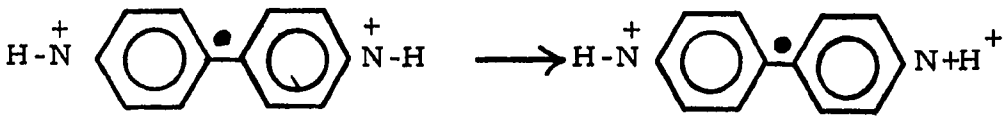
up to the potential region of the adsorption prewave. At potentials more negative than the adsorption prewave, the current-time curve at a given potential is oscillatory. The observed current-time curve resembles that of an underdamped current-time curve of an RC network superimposed upon a mass transport current time curve. As the electrode potential is made more negative, the time constant of the current oscillation increases. At 50 mv past the prewave the oscillations are damped out in about one minute, while 10 mv past the potential of the prewave the oscillations are damped out in just less than 10 seconds.

After imposing the potential, the first oscillation exceeds 500 μa cathodic current while on the first downward spike of the oscillatory current a net anodic current flows. After the oscillations have been damped out, a potential step as small as 1 mv results in similar but less violent oscillations. The direction of the first current spike is cathodic for a further 1 mv cathodic polarization while an initial anodic current displacement is observed for a 1 mv anodic potential step. When the oscillations resulting from these 1 mv potential steps have been damped out, the remaining mass transport current is virtually unaltered.

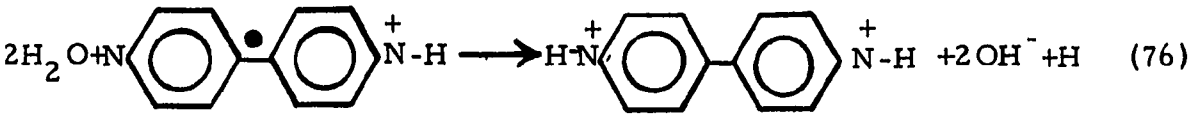
The rationalization of the observed ESR signal as a function of time, potential and extent of electrolysis is not unambigious. Chemical reactions producing free radical or slow desorption of sorbed free radical could be the cause of the increase in ESR signal after terminating electrolysis. Of the two possibilities the most probable is a chemical reaction similar to (71) proposed for the methyl viologen system, but no evidence for such a

reaction in the case of 4,4'-dipyridyl system can be presented at this time.

The first order decay of the 4,4'-dipyridylium radical ion at the foot of the polarographic wave, can be rationalized in terms of reactions (75) and (66) below:



(75)



(76)

It is suggested that once the radical looses a proton, thus becoming unsymmetrical, it is a powerful reductant and is sufficiently strong to oxidize water. The radical produced by the attack on the solvent should be highly unstable and should decay quite rapidly. The departure from first-order kinetics can be ascribed to a reaction like (71) proposed above for the growth of the ESR signal at the more cathodic potentials or to a slow desorption. At the less cathodic potentials the quantity of doubly reduced species XX is much less and therefore, reactions between it and unreduced 4,4'-dipyridylium ion XVIII should be less important.

VI. CONCLUSIONS

It has been shown that free radicals play an important role in several organic electrochemical reductions.

The observation of a free radical in the case of the four-electron reduction of several aromatic nitrocompounds illustrates the point that this reduction process involves at least two slow consecutive one-electron steps. At potentials which correspond to the foot of the polarographic wave, the rate of the first electron addition must be comparable to the rate of the second electron addition. The mechanism proposed, (53), (54), (5) and (6), is an example of steps (23), (24), (27) and (28) in the general scheme proposed by Elving and Pullman [3]. The radical which is observed must therefore be an electrochemical intermediate which has escaped from the electrode surface.

The electrochemical reduction of 4,4'-dipyridylium ion is another example of two consecutive one-electron additions, (73) and (74). Electrode potential-ESR intensity data show that the final product of the electrolysis is not the free radical, but it is a more reduced state, probably the two electron product. In terms of the general mechanism considered earlier (23) to (32), this reduction is an example of reactions (23), (24), (26) and (27).

The electrochemical reduction of N-methylpyridinium ion does not yield the expected free radical, but rather the radical observed is due to a condensed product. This observed radical is not directly produced by an electrochemical reduction, but it results from a homogeneous chemical

reaction. The several initial steps in the reduction of N-methylpyridinium ion are consistant with reactions (23), (24) and (25) in the general scheme of Elving and Pullman[3].

In contrast to the four electron reduction of both benzenoid and aliphatic nitrocompounds, the nitroferrocene reduction at a dropping mercury electrode is a six electron process. This multi-electron reduction is a diffusion controlled irreversible process. The pH dependence of the polarographic half-wave for nitroferrocene reduction is the same as that for benzenoid nitrocompounds, but the $E_{\frac{1}{2}}$ of the nitroferrocene reduction at the same pH is always more negative than that for nitrobenzene or most monosubstituted nitrobenzenes. The failure to observe an electrochemically stable hydroxylamine oxidation state is a fundamental difference between nitrobenzene and nitroferrocene. In the electrochemical-ESR experiments the failure to observe a large steady state concentration of a free radical intermediate for nitroferrocene suggests that the second electron in the nitroferrocene reduction is added rapidly with respect to the first electron. This is in contrast to the observed radicals for both benzenoid and aliphatic nitrocompounds. The magnitude of the observed nitrogen coupling constant for nitroferrocene indicates that nitroferrocene has a significant aromatic character.

BIBLIOGRAPHY

1. Heyrovsky, J., Chem. Listy. 16, 256 (1922).

2. Evans, M. G. and Hush, N. S., J. chim. phys. 49, C195 (1952).

3. Elving, P. J. and Pullman, B., Advances in Chemical Physics 3, 1 (1961).

4. Koutecky, J. Chem. Listy. 47, 323 (1953).

5. Koutecky, J., "Soviet Electrochemistry, vol I, Kinetics and Polarography," Consultants Bureau, New York, 1961, p. 177, (English translation).

6. Reinmuth, W. H., Anal. Chem. 32, 1514 (1960).

7. Ibid., 33, 322 (1961).

8. Laitinen, H. A. and Wawozonek, S., J. Am. Chem. Soc. 64, 1765 (1942).

9. Clark, R. P., Ph.D. Thesis, University of Illinois, 1961.

10. Korshounov, I.A and Kirillova, A. S., Zhur. Obshchei Khim. 18, 785 (1948).

11. Testa, A. C., Ph.D Thesis, Columbia University, 1961.

12. Kemula, W. and Kublik, Z., Roczniki Chem. 32, 941 (1958).

13. Maki, A. H. and Geski, D. H., J. Am. Chem. Soc. 83, 1852 (1961).

14. Piette, L. H., Ludwig, P. and Adams, R. N., J. Am. Chem. Soc. 83, 3909 (1961).

15. Ibid., Anal. Chem. 34, 916 (1962).

16. Tompkins, P. C. and Schmidt, C. L. A., Univ. of Calif. Pub. Physiol. 8, 237 (1943).

17. Leach, S. J. and Baxendale, J. H., Aust. J. Chem. 6, 395 (1953).

18. Emmert, B., Ber. 42, 1997 (1909).

19. Schwarz, W. M., Kosower, E. M. and Shain, I., J. Am. Chem. Soc. 83, 3164 (1961).

20. Pasternak, R., Helv. Chem. Acta 31, 753 (1948).

21. Swann, S. Jr. and Nelson, G. H., Trans. Electrochem. Soc. 67, 201 (1935).

22. Suzuki, M. and Elving, P., J. Phys. Chem. 65, 391 (1961).

23. Delahay, P., "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, 1954, p. 217.

24. Laitinen, H. A. and Kolthoff, I. M., J. Am. Chem. Soc. 61, 3344 (1939).

25. Laitinen, H. A., Trans. Electrochem. Soc. 82, 289 (1942).

26. Shain, I. and Martin, R., J. Phys. Chem. 65, 254 (1961).

27. Delahay, P., op. cit., p. 46.

28. Delahay, P., op. cit., p. 72.

29. Laitinen, H. A., "Chemical Analysis, "McGraw-Hill Book Co. Inc., New York, 1960, p. 306.

30. Delahay, P., op. cit., p. 87.

31. Beronius, P., Z. Elektrochem. 66, 17 (1962).

32. Austen, D. E. G., Given, P. H., Ingram, D. J. E. and Peover, M. E., Nature 182, 1784 (1958).

33. Ingram, D. J. E., "Free Radicals as Studied by Electron Spin Resonance," Butterworths Scientific Publications, London, 1958.

34. Weisman, S. I., J. Chem. Phys. 25, 890 (1956).

35. Coulson, C. A., "Valence," University Press, Oxford, 1953, p. 312.

36. Weissman, S. I., J. Chem. Phys. 25, 764 (1956).

37. Berzins, T. and Delahay, P., J. Am. Chem. Soc. 75, 5716 (1953).

38. Heyrovsky, J. and Ilkovic, D., Collection Czechoslov. Chem. Commun. 7, 198 (1935).

39. Kelley, M. T., Jones, H. C. and Fischer, D. J., Anal. Chem. 31, 1475 (1959).

40. Blum, W. and Hogdson, G. B., "Principles of Electroplating and Electroforming," 3rd ed., McGraw-Hill Book Co. Inc., New York, 1949.

41. Meites, L., "Polarographic Techniques", Interscience Publishers, Inc., New York, 1955, p. 22.

42. Prescott, A. B., J. Am. Chem. Soc. 18, 91 (1896).

43. Grubert, H. and Rinehart, K. L. Jr., Tetrahedron Letters, 1959, 1617.

44. Thiele, J., Ber. 33, 667 (1900).

45. Lingane, J. J., "Electroanalytical Chemistry" 2nd Ed. Interscience Publishers, Inc., New York, 1958, p. 461.

46. Geske, D. H., and Maki, A. H., J. Am. Chem. Soc. 82, 2671 (1960).

47. Wertz, J. E. and Vivo, J. L., J. Chem. Phys. 23, 2441 (1955).

48. Kethel, C., "Elementary Statistical Physics," J. Wiley and Son, New York, 1958, p. 155.

49. Kolthoff, I. M. and Lingane, J. J., "Polarography" 2nd Ed., Interscience Publishers, Inc., New York, 1952, p. 746.

50. Testa, A. C. and Reinmuth, W. H., J. Am. Chem. Soc. 83, 784 (1961).

51. Petru, F., Collection Czechoslov. Chem. Communs. 12, 620 (1947).

52. Stewart, P. E. and Bonner, W. A., Anal. Chem. 22, 793 (1950).

53. Mitter, E. W., Arnold, A. P., and Astle, M. J., J. Am. Chem. Soc. 70, 3971 (1949).

54. Pauson, P., Quart. Revs. (London) 9, 391 (1955).

55. Rausch, M. D., Vogel, M. and Rosenberg, H., J. Chem. Ed. 34, 268 (1957).

56. Schlogl, K., Osterr. Chem. Ztg. 59, 93 (1958).

57. Rausch, M. D., Fischer, E. O. and Grubert, H., J. Am. Chem. Soc. 82, 76 (1960).

58. Helling, J. F., and Shechter, H., Chem. and Ind. 1959, 1157.

59. Tiroufelt, J., Bochard, J. and Delepine, M., Compt. rend. 250, 1861 (1960).

60. Page, J. and Wilkenson, G., J. Am. Chem. Soc. 74, 6149 (1952).

61. Kiuwane, T. K., Bublitz, D. E. and Hoh, G., J. Am. Chem. Soc. 82, 5811 (1960).

62. Hoh, G., McEwen, W. and Kleinberg, J., J. Am. Chem. Soc. 83, 3949 (1961).

63. Tirouflet, J. and Boichard, J., Bull. soc. chim. Fr. 1960, 4.

64. Tirouflet, J. and Boichard, J., Bull.soc. chim. Fr. 1960, 1032.

65. Komenda, J. and Tirouflet, J., Compt. rend. 254, 3093 (1962).

66. Kolthoff, I. M. and Lingane, J. J., op. cit., p. 85.

67. Kolthoff, I. M. and Lingane, J. J., op. cit., p. 63.

68. Kolthoff, I. M. and Lingane, J. J., op. cit., p. 246.

69. Geski, D. H. and Ragle, J. L., J. Am. Chem. Soc. 83, 3532 (1961).

70. Michaelis, L., Hill, E S., J. Gen. Physiol. 16, 859 (1933).

71. Brium, F., Heineken, F. W., Brium, M. and Zahlen, A., J. Chem. Phys. 36, 2783 (1962).

72. Elofson, R. M., and Edsberg, R. L., Can. J. Chem. 35, 646 (1957).

73. Colichman, E. L. and O'Donovan, P. A., J. Am. Chem. Soc. 76, 3588 (1954).

74. Bredig, G., Z. physik. Chem. 13, 191 (1894).

75. Schwarz, W. M., Ph.D. Thesis, University of Wisconsin, (1961).

76. Enke, C., Ph.D. Thesis, University of Illinois, (1959).

77. Michaelis, L., Chem. Rev. 16, 243 (1935).

78. Michaelis, L., and Schubert, M. P., Chem. Rev. 22, 437 (1938).

79. Zahlen, A. B., and Linnell, R. H., J. Am. Chem. Soc. 77, 6207 (1955).

80. Johnson, C. S., Visco, R. E., Gutowsky, H. S., and Hartley, A. M., J. Chem. Phys., (in press).

81. Falqui, M. T., and Secci, M., Ann. chim. (Rome) 48, 1168 (1958).

82. Krumholz, P., J. Am. Chem. Soc. 73, 3487 (1951).

VITA

Mr. Visco was born in New York City on April 9, 1934. He moved to Chicago, Illinois in October 1945 and graduated from Our Lady of the Angels Grammar School in that city. He attended St. Mel. High School in Chicago, and graduated in June 1951. Mr. Visco attended the University of Wisconsin and was awarded a Bachelor of Science Dgree with a major in chemistry in June, 1955. He remained at the University of Wisconsin and received a Master of Science with a major in physical chemistry in August, 1957.

Mr. Visco entered the United States Army upon graduation with the rank of Second Lieutenant. He served in the U.S. Army Chemical Corps and was discharged August 27, 1959 with the rank of First Lieutenant.

Mr. Visco entered the graduate school of the University of Illinois in September, 1959. His major was analytical chemistry with minors in physical chemistry and mathematics.

On August 7, 1957 he married the former Miss Margaret O'Neil of Detroit, Michigan. They have two children, Robert Edward, Jr., and William Mark.